The 81st Fujihara seminar
2024.6.3. 16:15-16:35

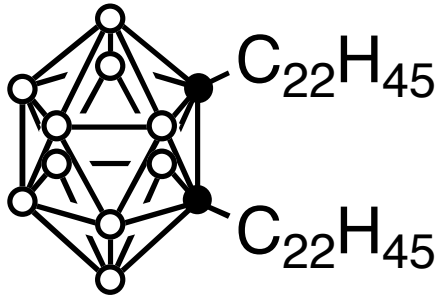
Quantitative Analysis Around Crystallization Phenomena via Molecular Electron Microscopy

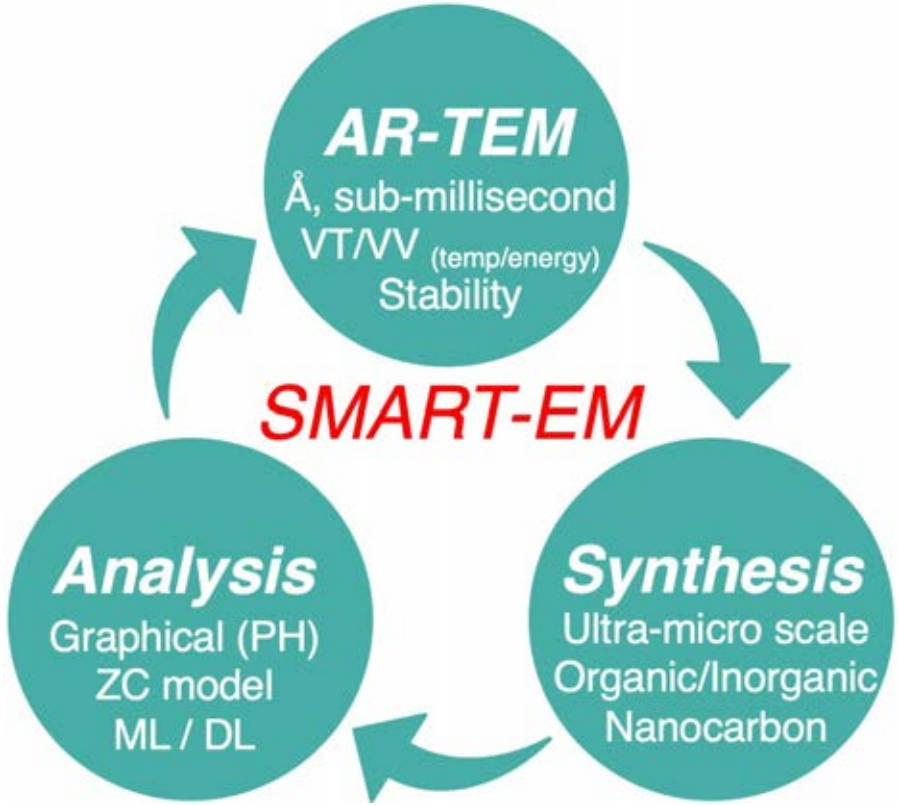
Takayuki NAKAMURO

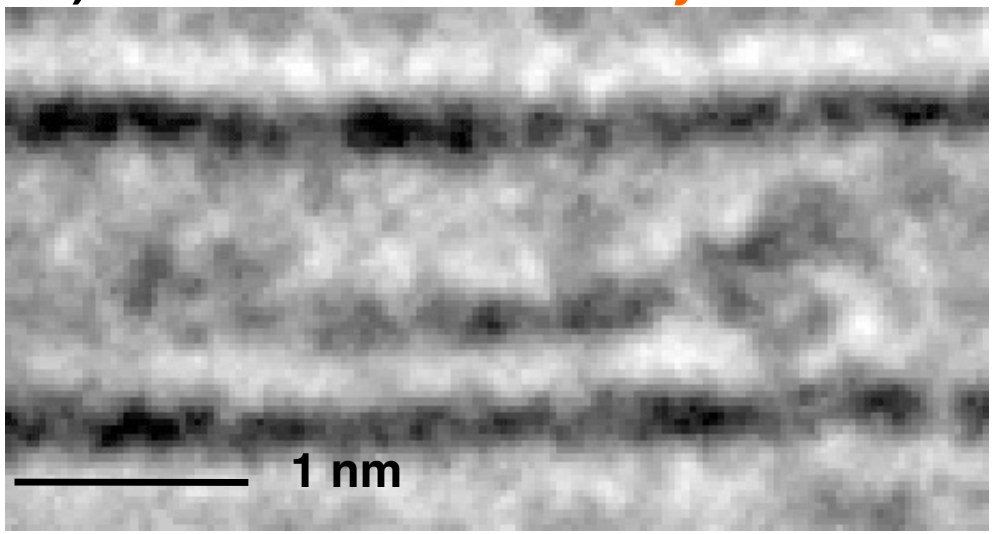
“Molecular Technology Innovation”
Presidential Endowed Chair

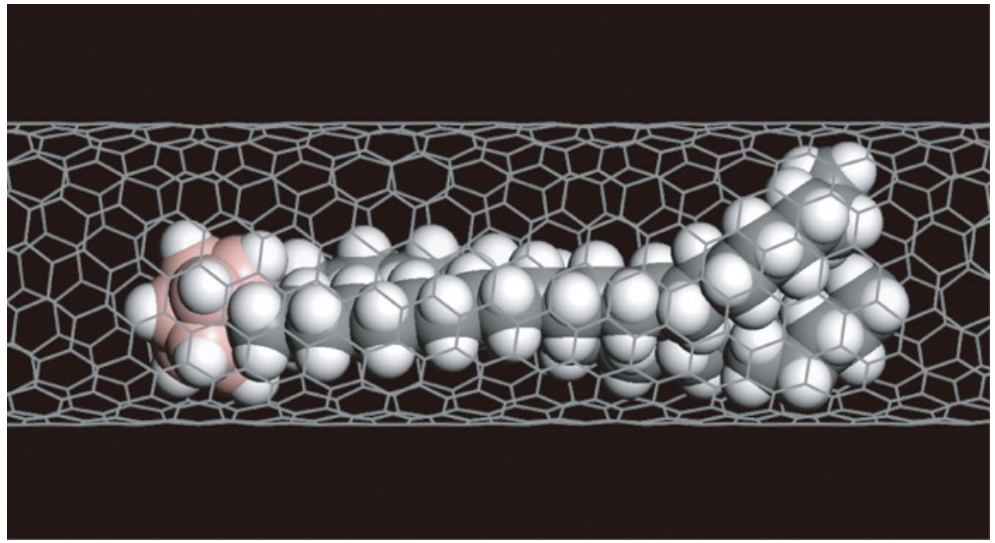
The First Movie of a Single Molecule in Motion

Single-Molecule, Atomic-Resolution Time-resolved Electron Microscopy (SMART-EM) or *Cinematic Chemistry*

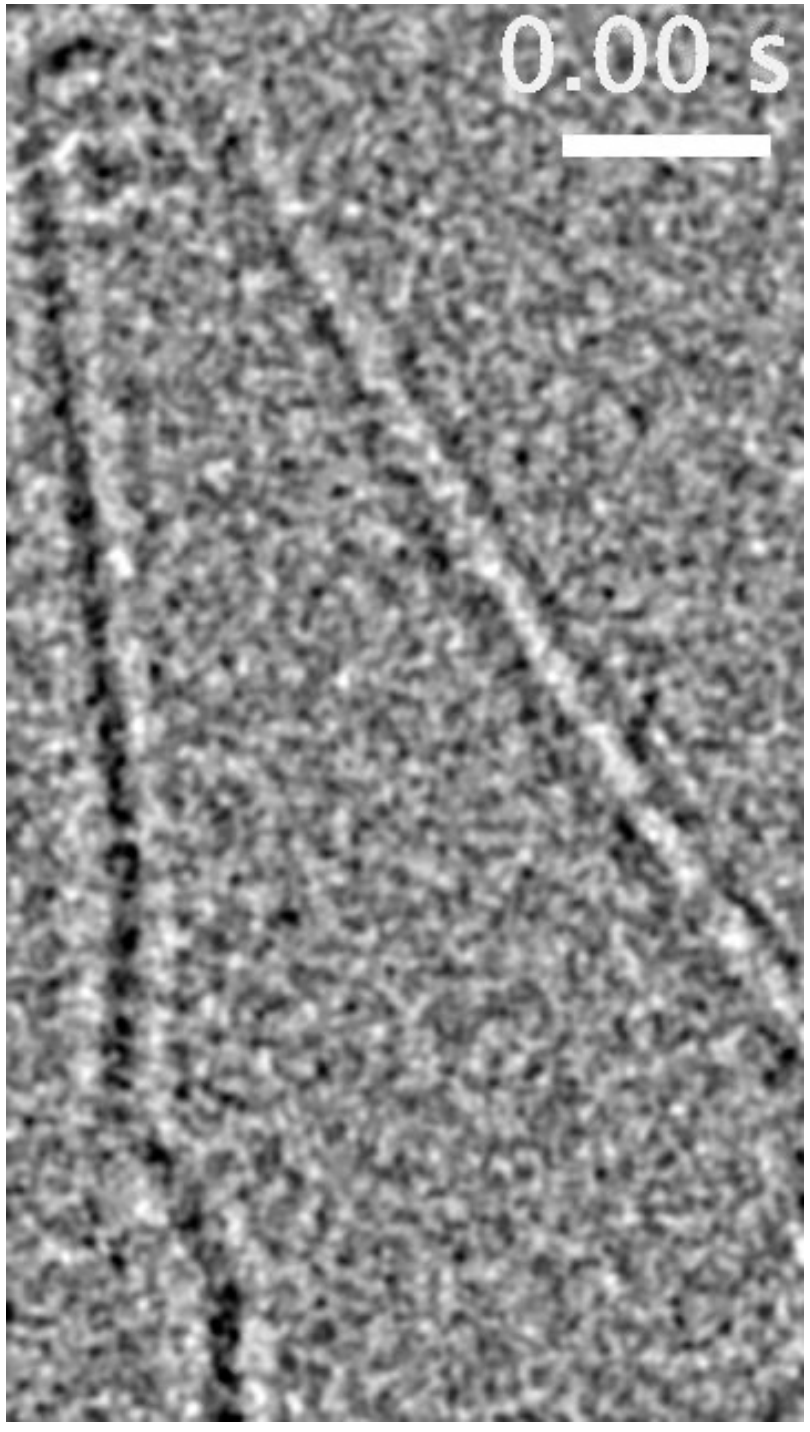




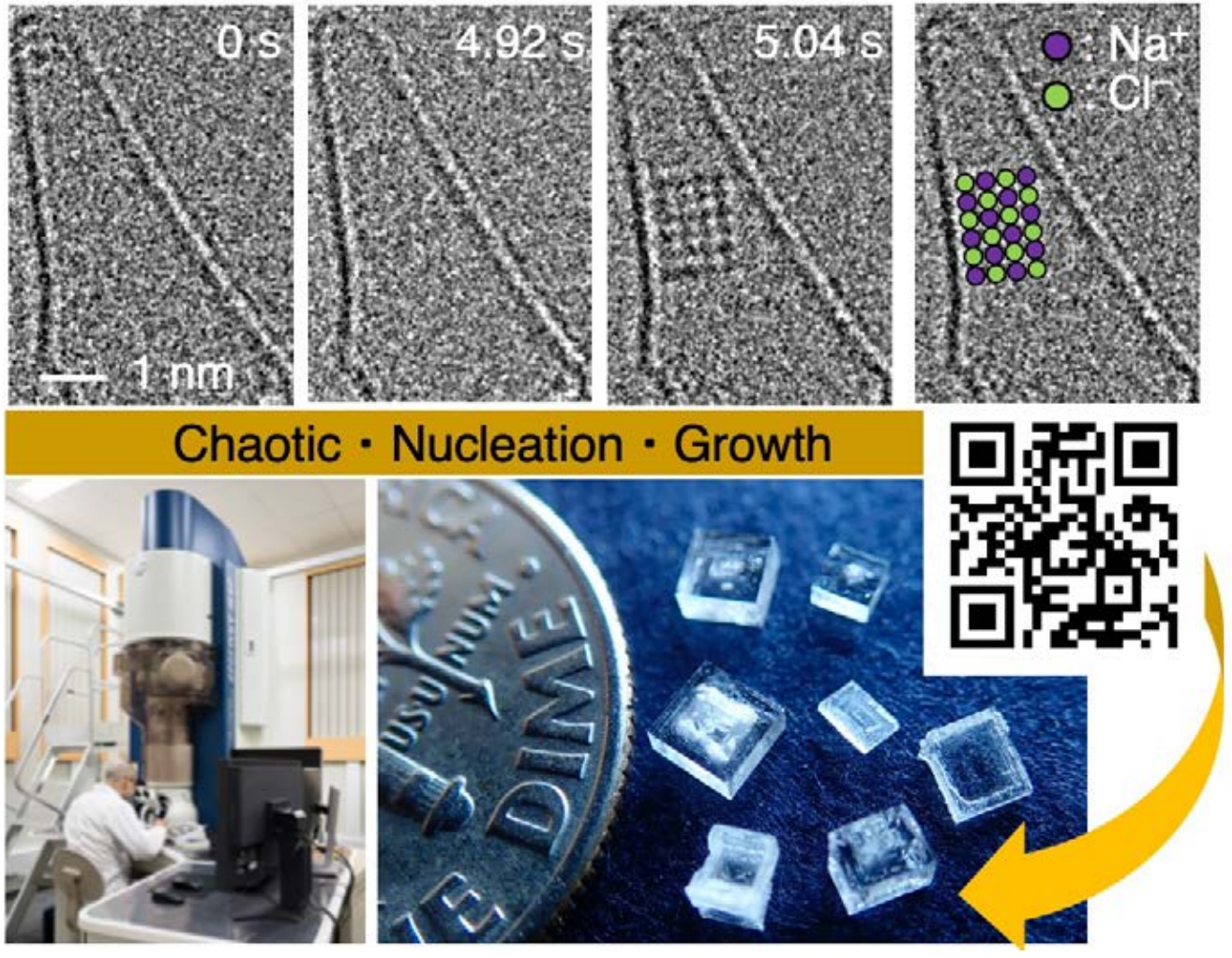




K. Suenaga, H. Isobe, E. Nakamura *et al. Science* **2007**, *316*, 853.



Capturing the Moment of Crystallization

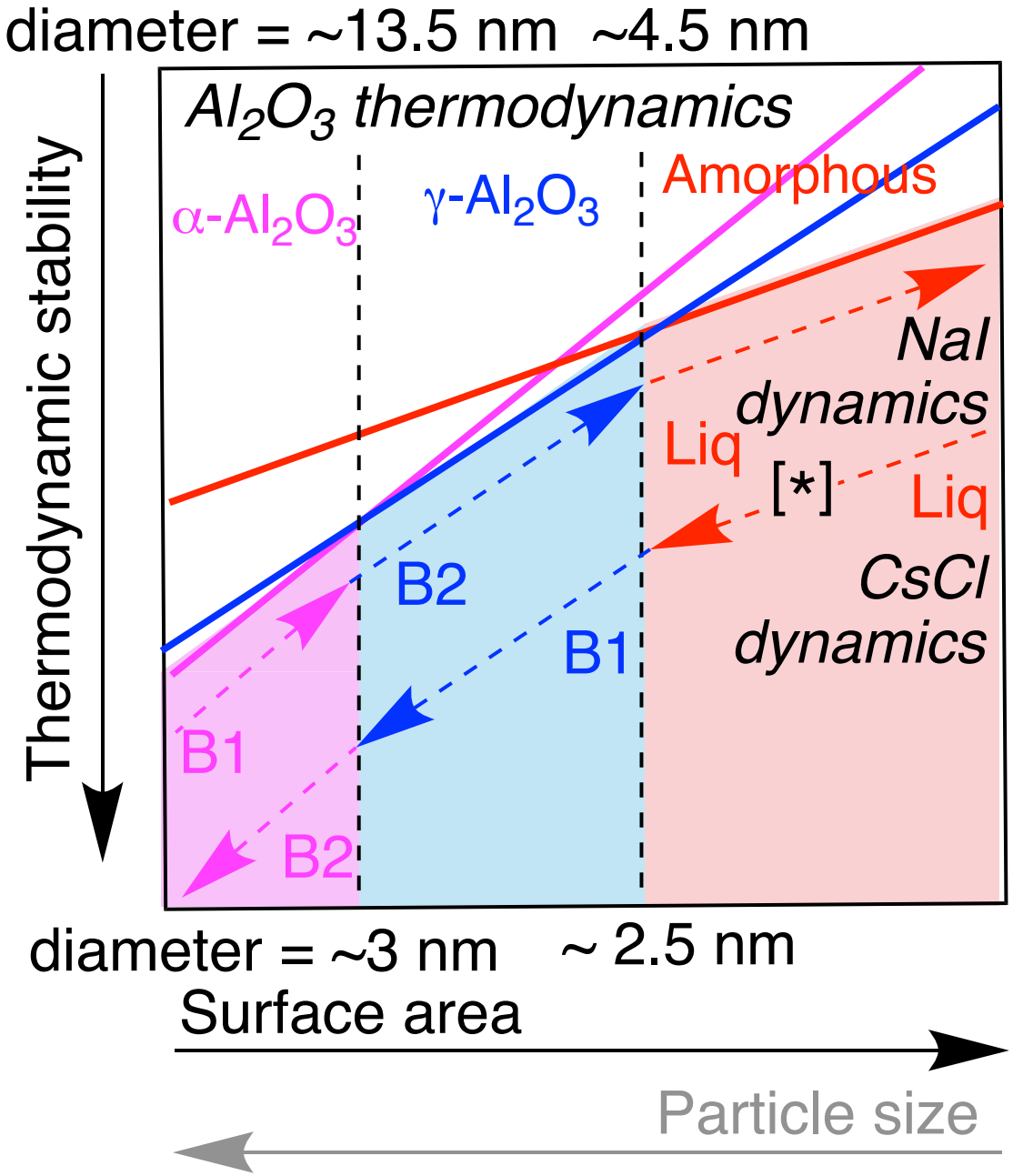


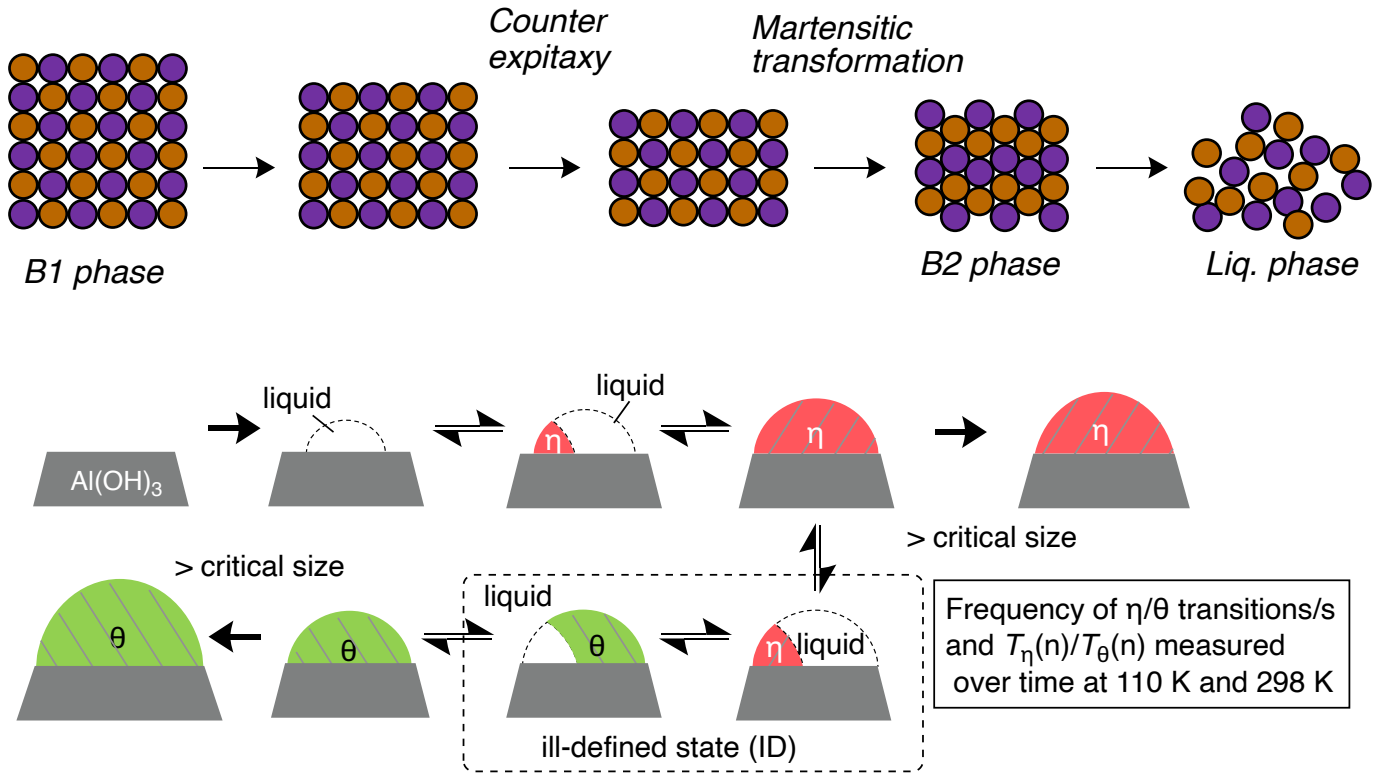
Presented in the pre-symposium

T. Nakamuro *et al. J. Am. Chem. Soc.* **2021**, *143*, 1763.

M. Sakakibara *et al. ACS Cent. Sci.* **2022**, *8*, 1704.

Topic: Size-dependent Polymorphism

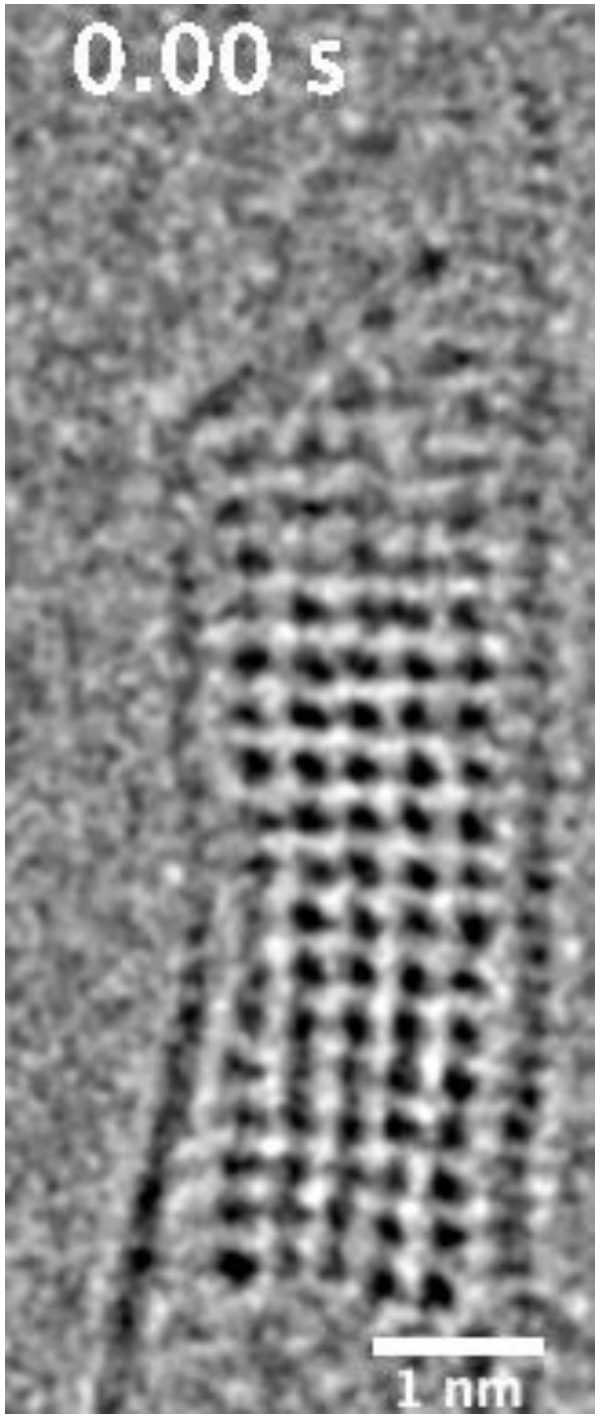


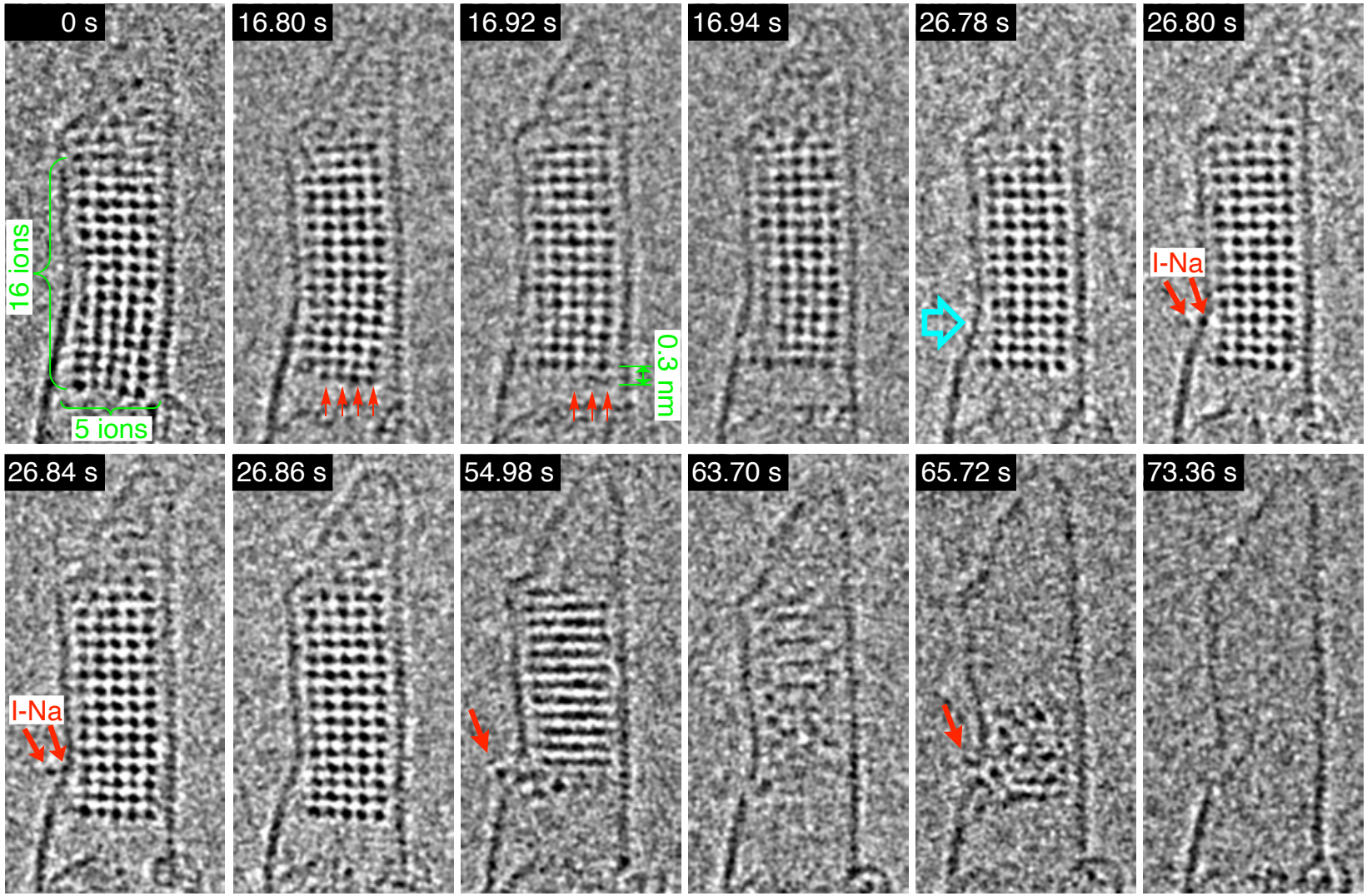


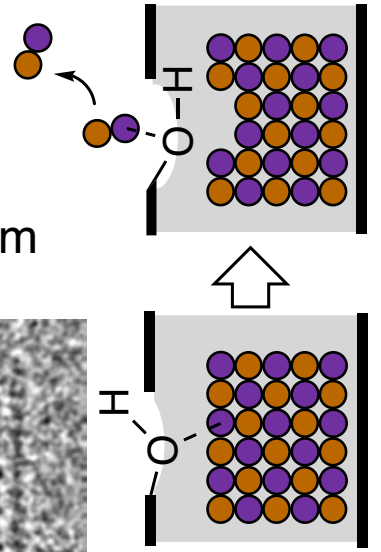
Additional: Micro-meter world

Search for Polymorphs Using *Nanotest Tube Method*

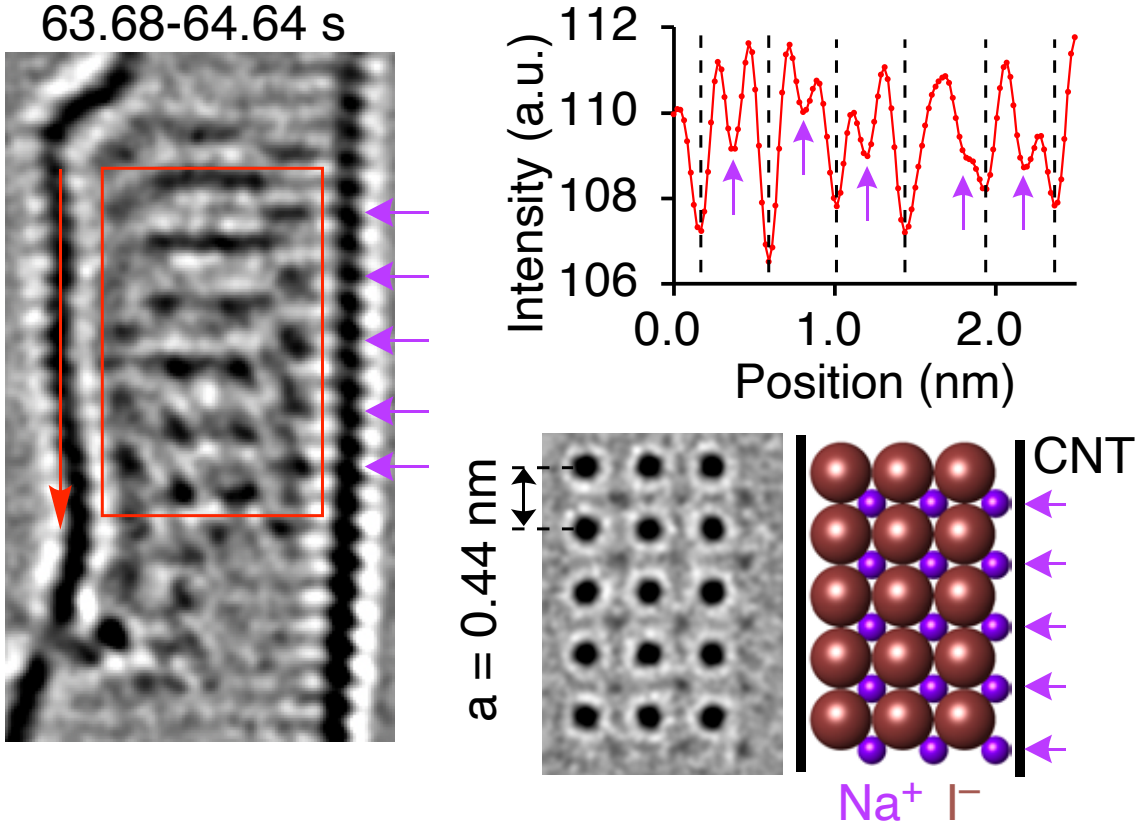
50 fps, EDR of 4.0 × 10^5 e^- nm^{-2} s^{-1}, 298 K, vacuum

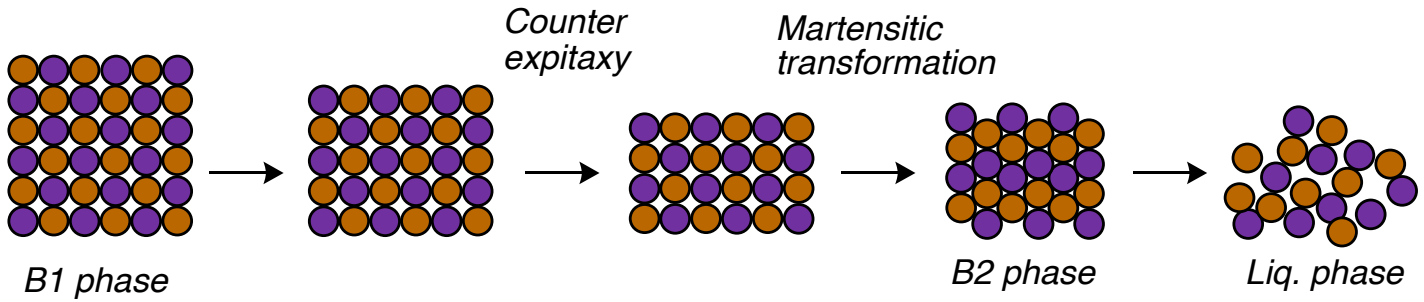




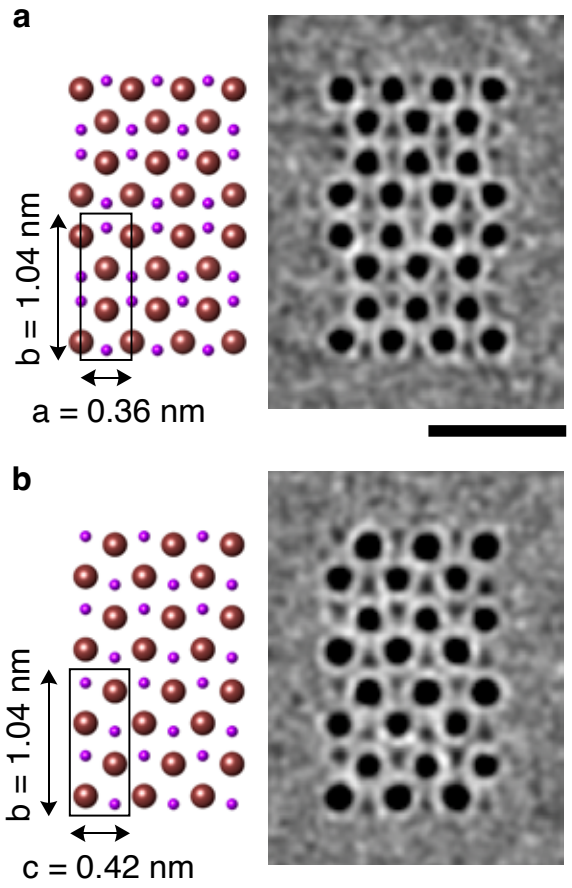


Structural Analysis of Unknown Polymorph



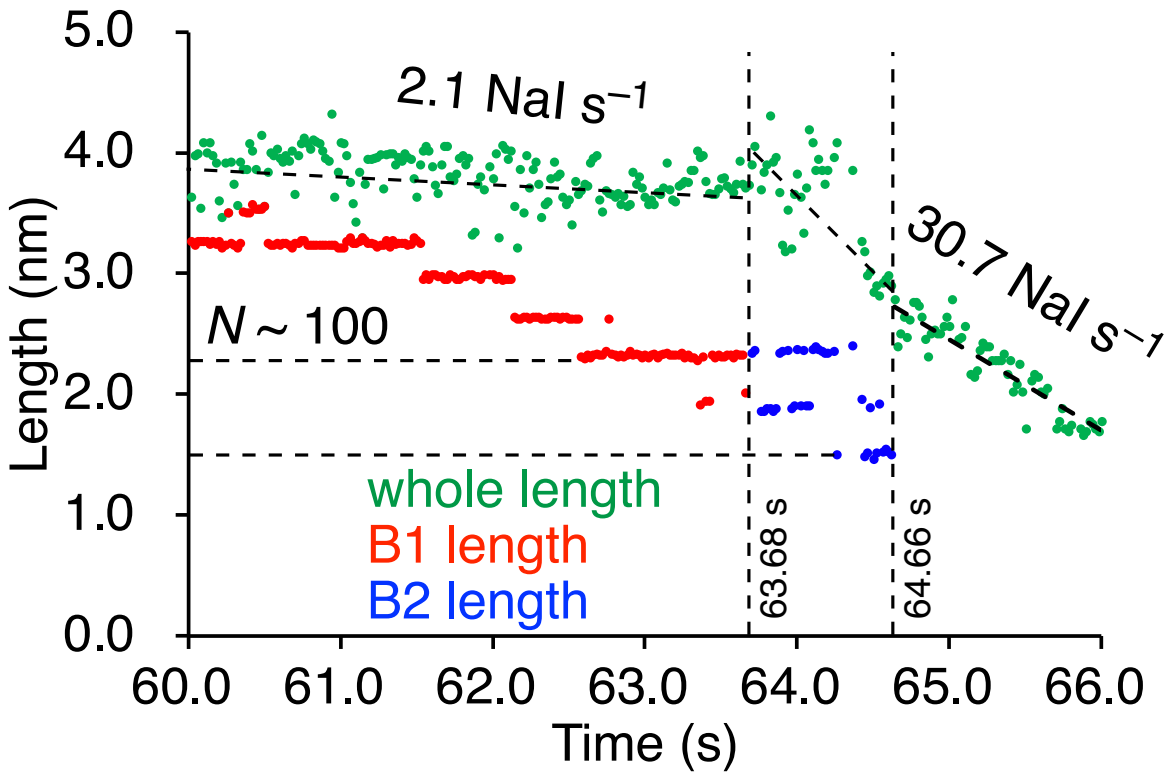


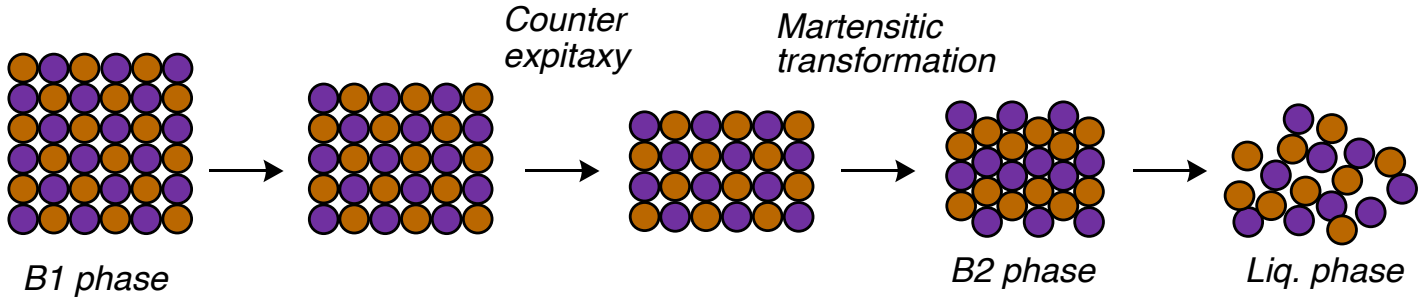
A. Navrotsky *et al.*, *Science* **1997**, *277*, 788.
M. Sakakibara *et al.*, *ChemRxiv (10.26434/chemrxiv-2024-ms4t7)*

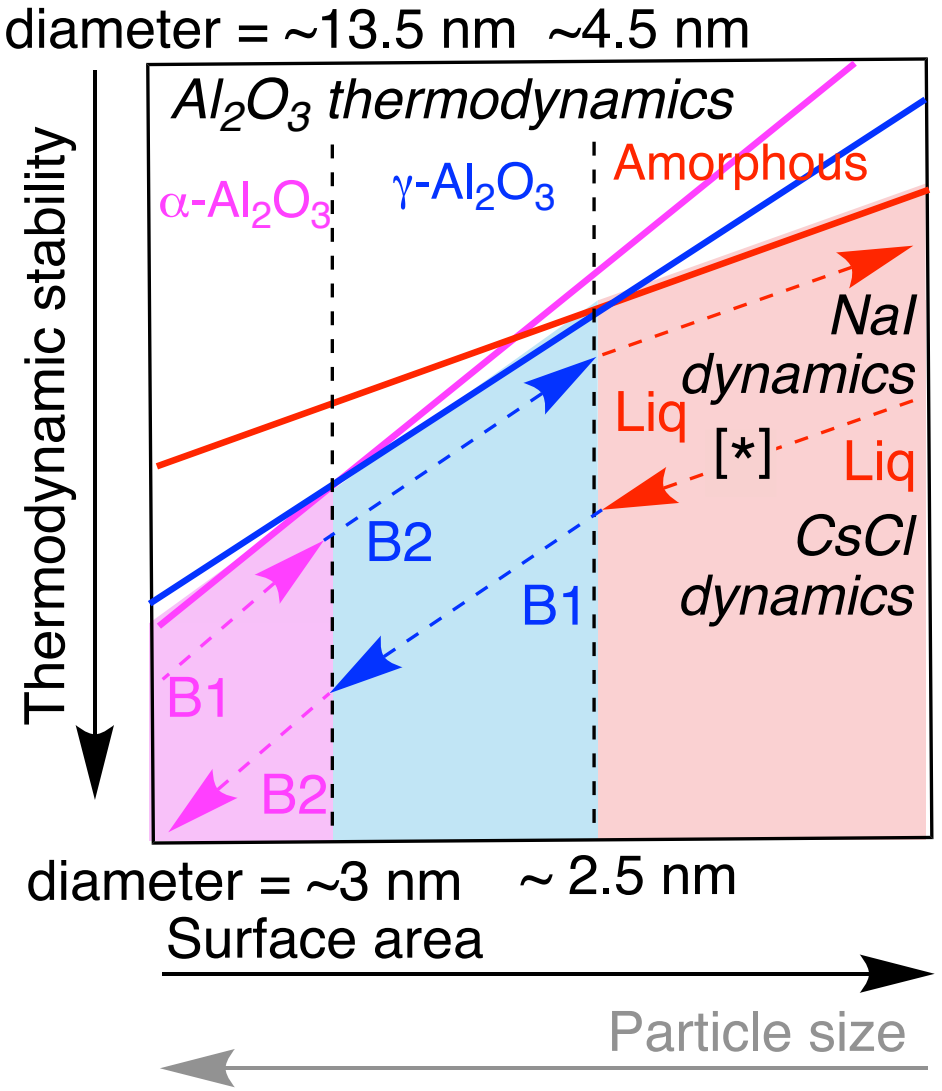


J. M. Léger *et al.*, *J. Phys.: Condens: Matter* **1998**, *10*, 4201.
(B33 structure at 40 GPa)

Stability of Nanocrystalline Polymorphs Reversed

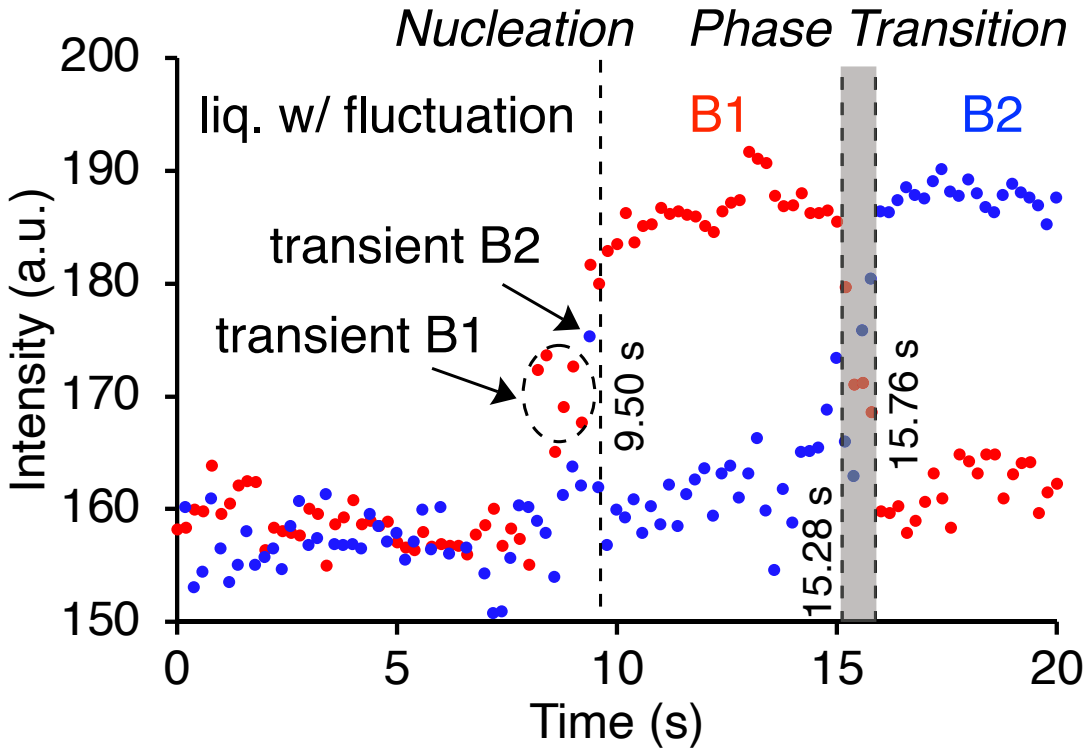


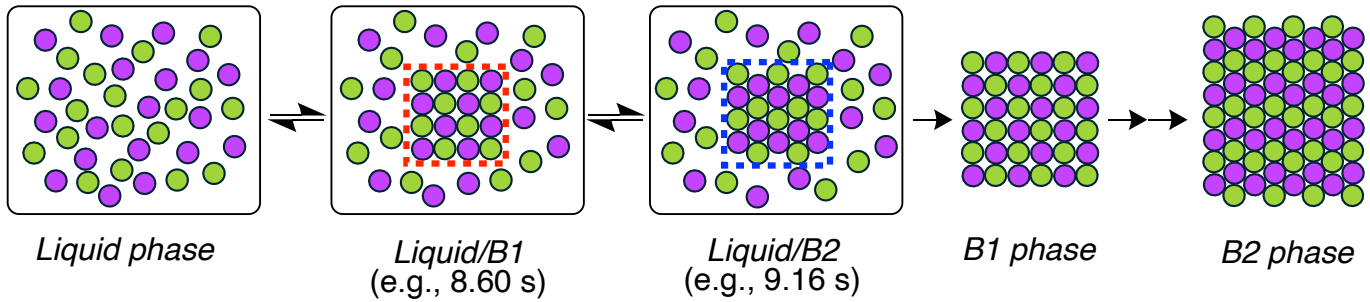




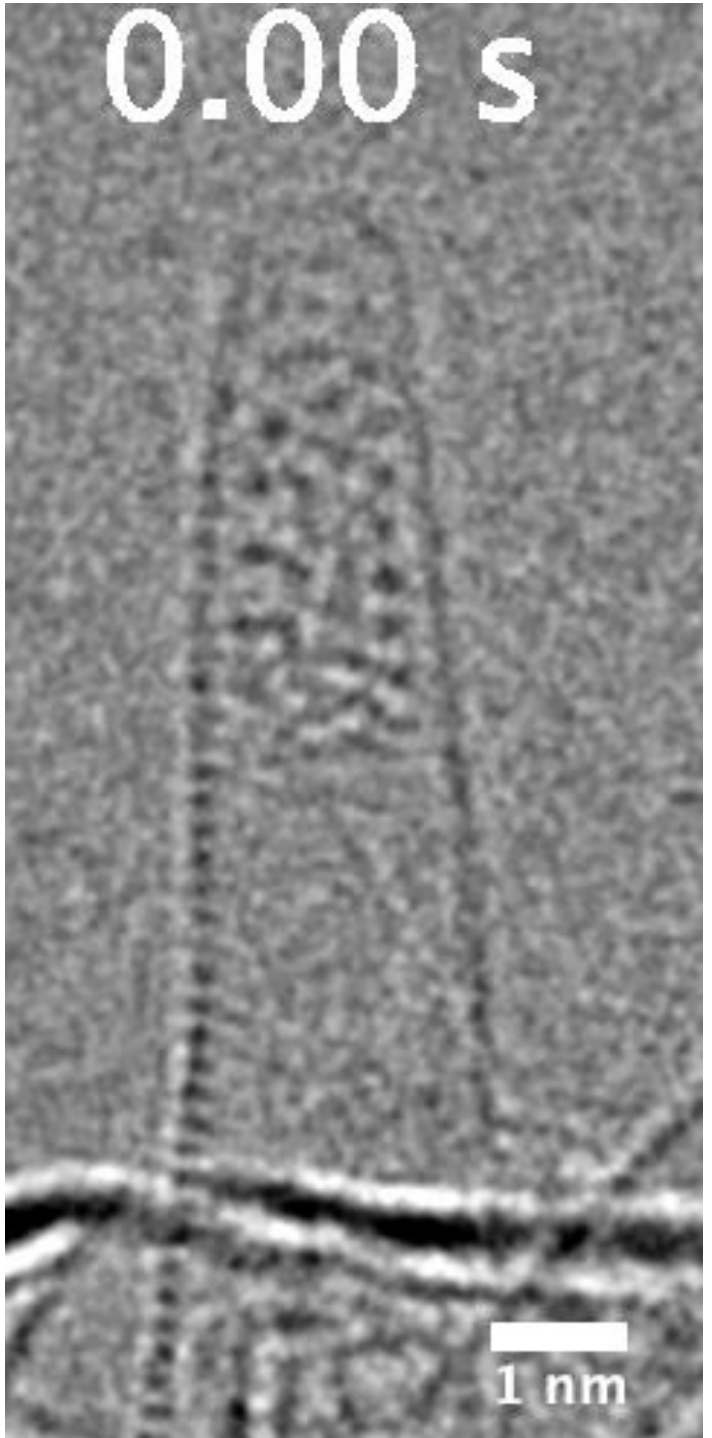
A. Navrotsky *et al.*, *Science* **1997**, *277*, 788.
M. Sakakibara *et al.*, *ChemRxiv (10.26434/chemrxiv-2024-ms4t7)*

CsCl Nucleates as NaCl-type

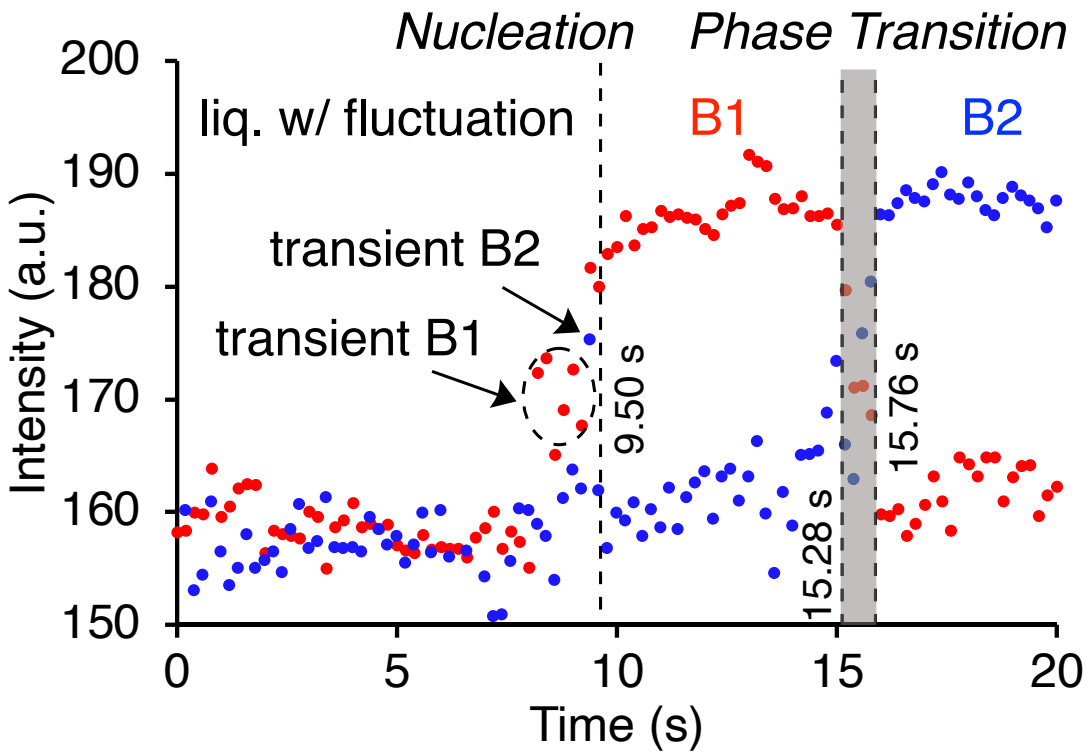


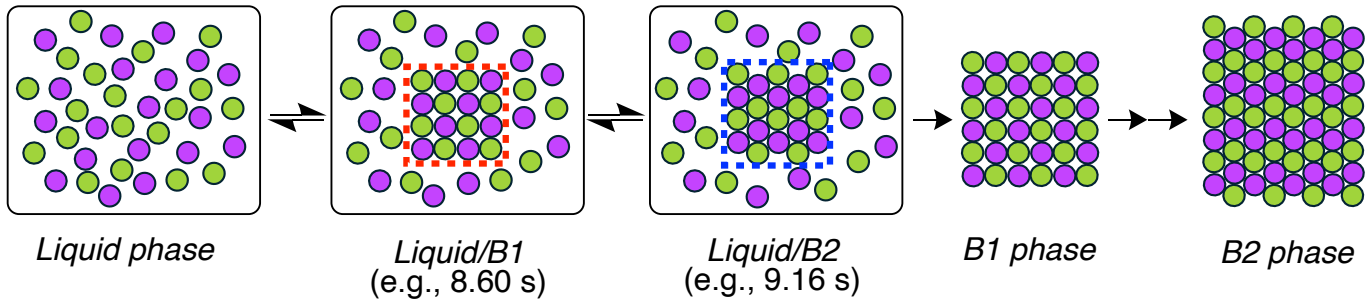


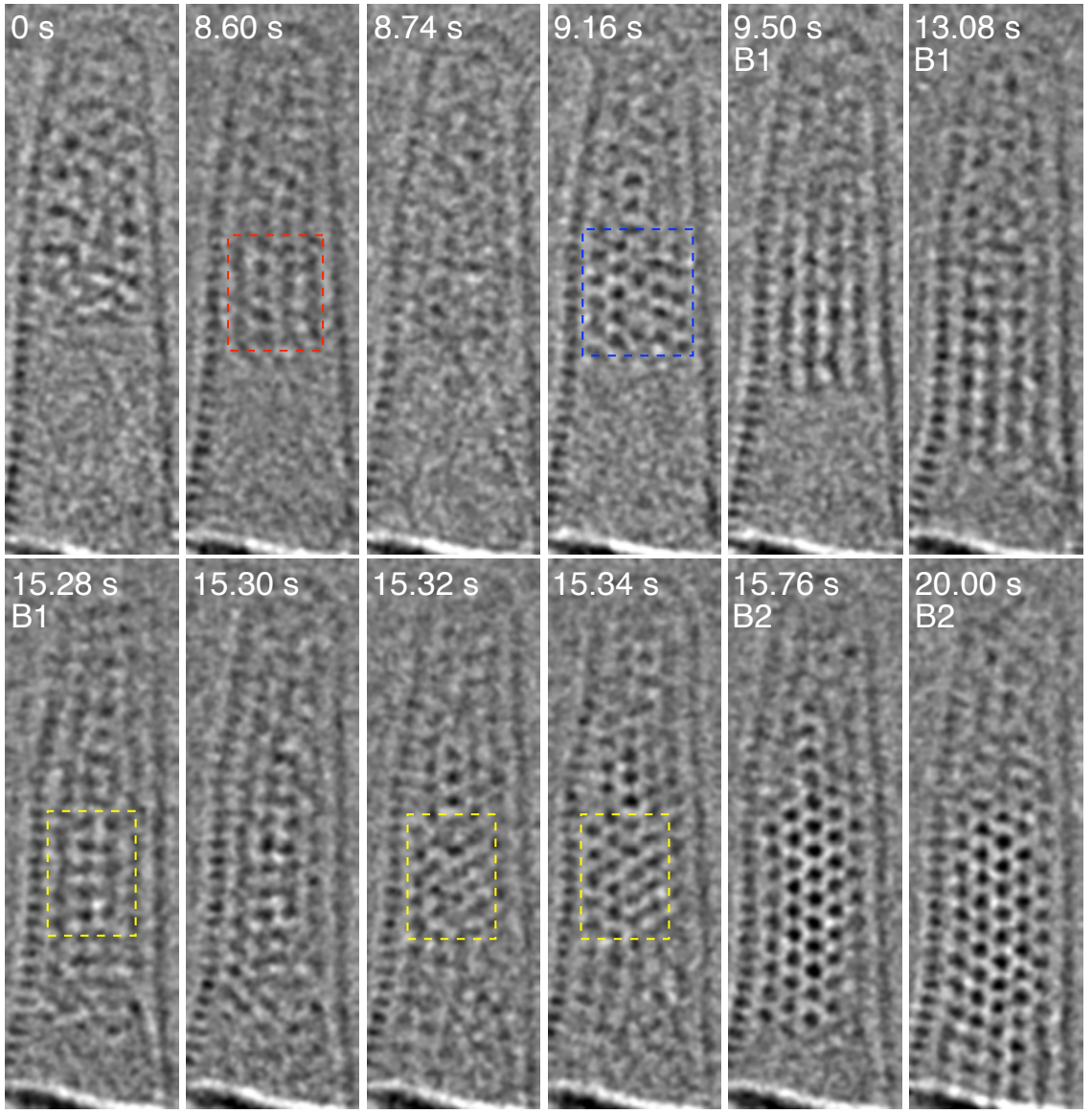
50 fps, EDR of 3.4 × 10^6 e^- nm^{-2} s^{-1}
298 K, vacuum



CsCl Nucleates as NaCl-type



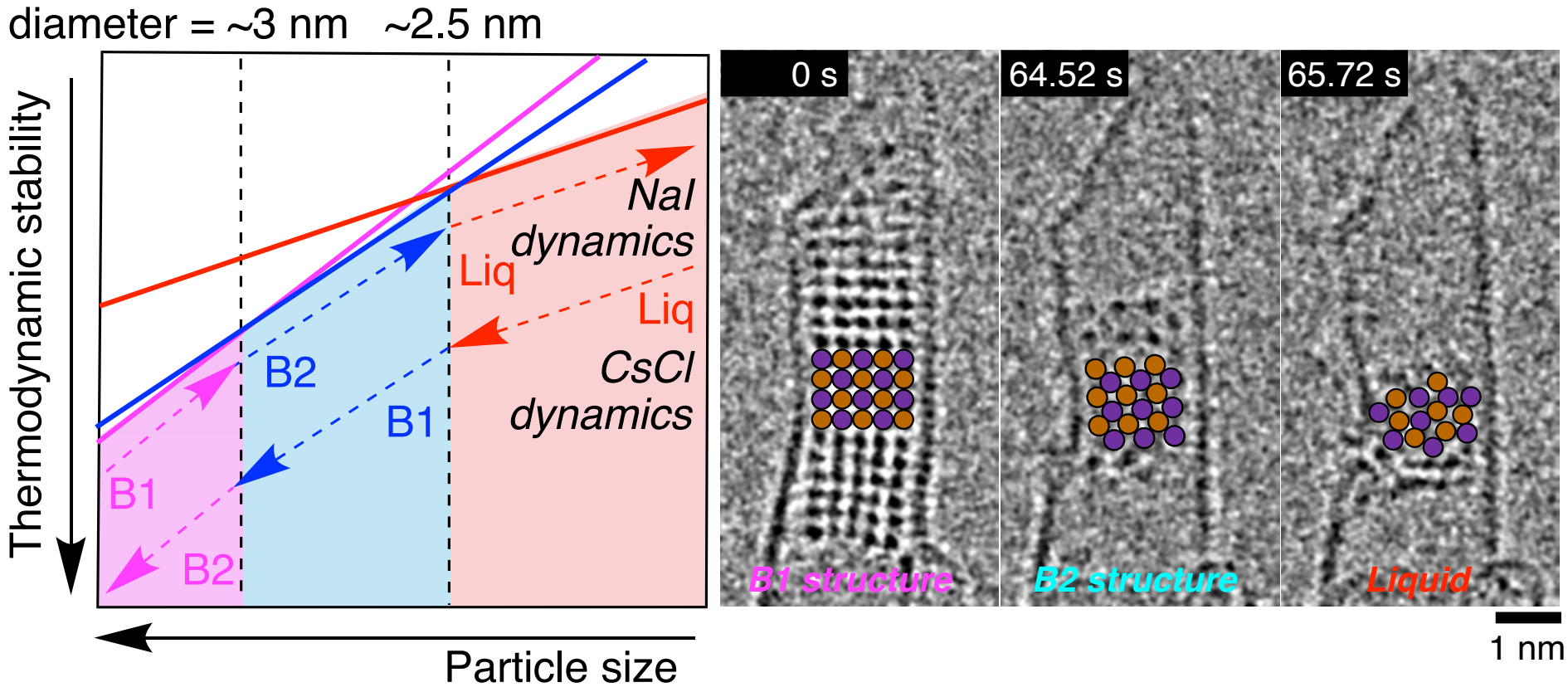




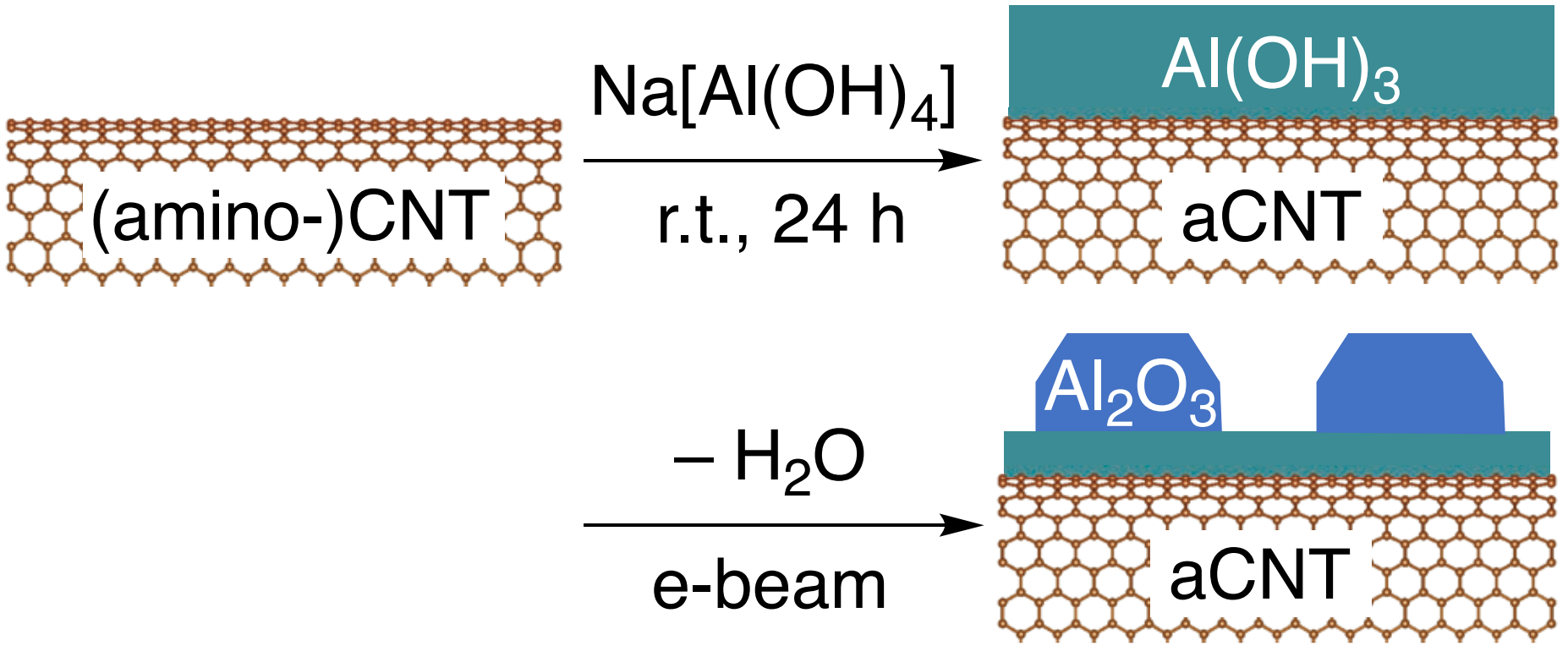
50 fps, EDR of 3.4 × 10^6 e^- nm^{-2} s^{-1}
298 K, vacuum

Summary of This Topic

- TEM direct imaging of nucleation/growth of nanocrystals enabled the exploration of its mechanism and size dependency in polymorphism.
- Nano-specific polymorphs can give us important insights for designing nanomaterials with unique structures.



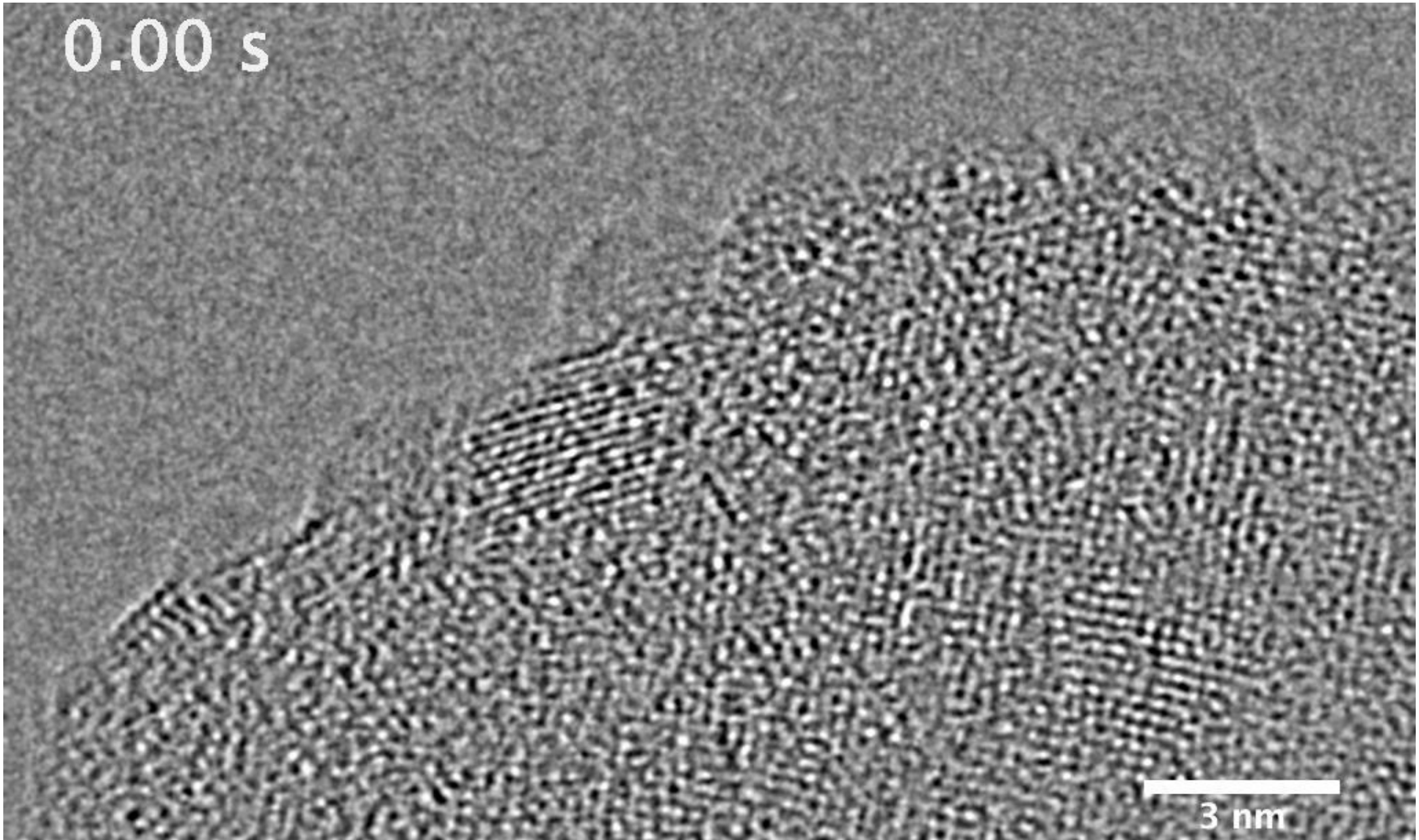
Chemical Coating: Unrestricted Observation Space



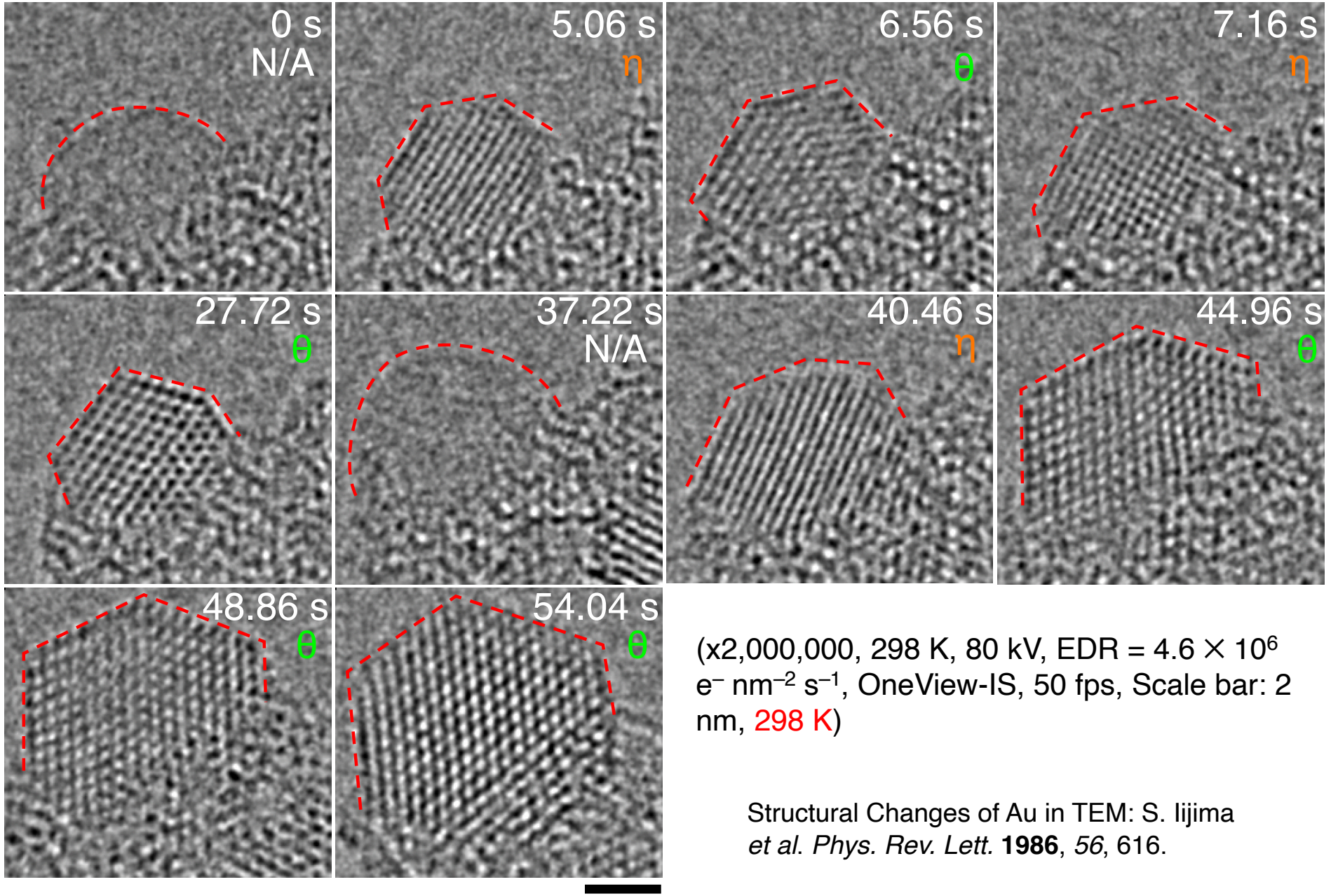
Analyzed by PXRD and TG-DTA

Insoluble $Al(OH)_3$ was deposited onto CNTs through hydrolysis & heterogeneous nucleation.

Al_2O_3 Formation under TEM Observation



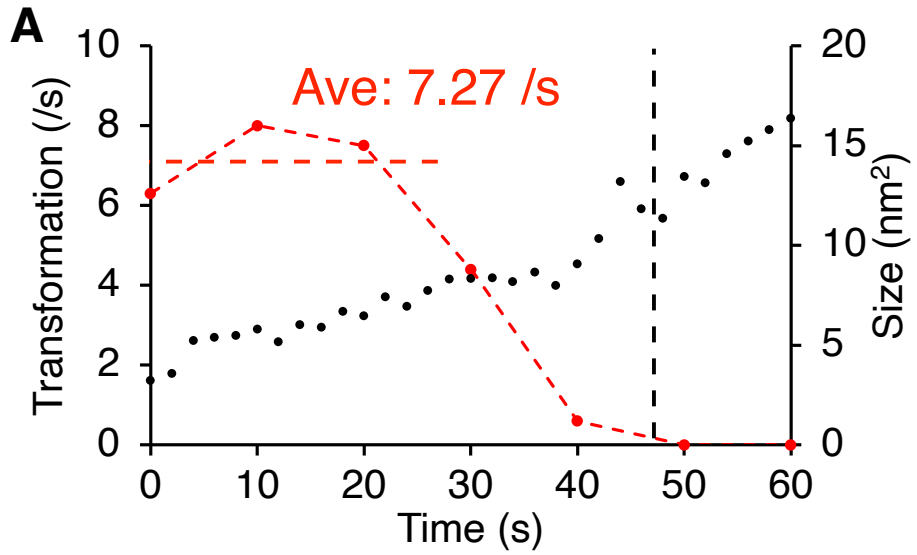
Polymorphism Is Not *Deterministic* But *Stochastic*

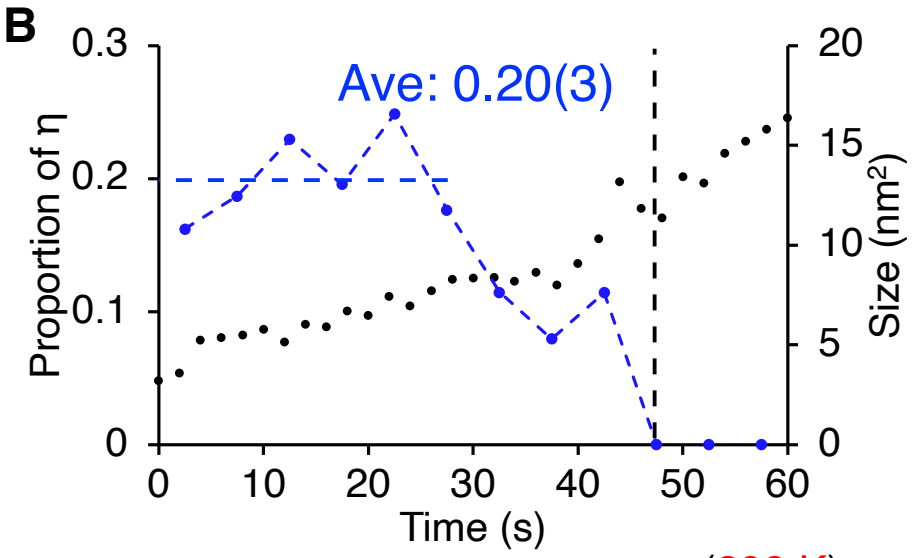


(x2,000,000, 298 K, 80 kV, EDR = 4.6 × 10^6 e^- nm^{-2} s^{-1}, OneView-IS, 50 fps, Scale bar: 2 nm, 298 K)

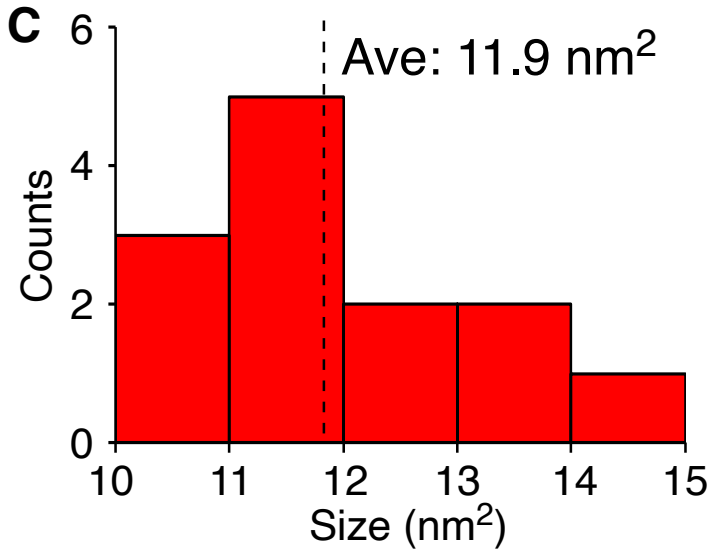
Structural Changes of Au in TEM: S. Iijima *et al. Phys. Rev. Lett.* **1986**, *56*, 616.

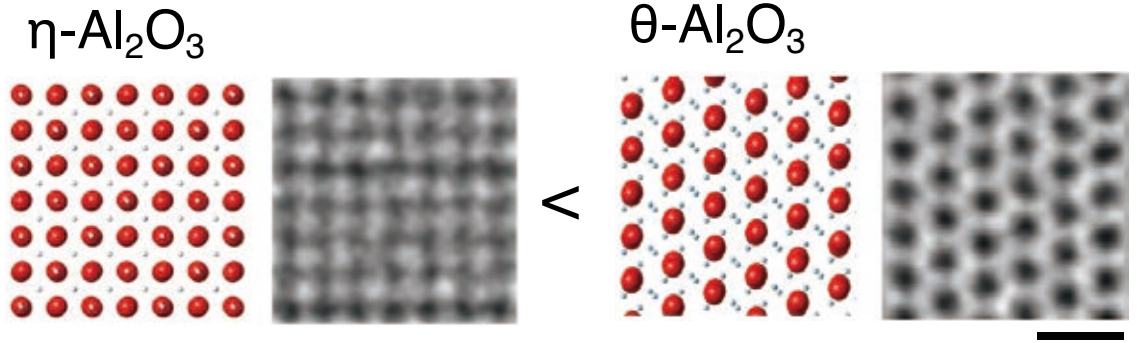
Time-Evolution of Structural Features





(298 K)





Stabler θ-Al_2O_3 became dominant in the late stage of nucleation.

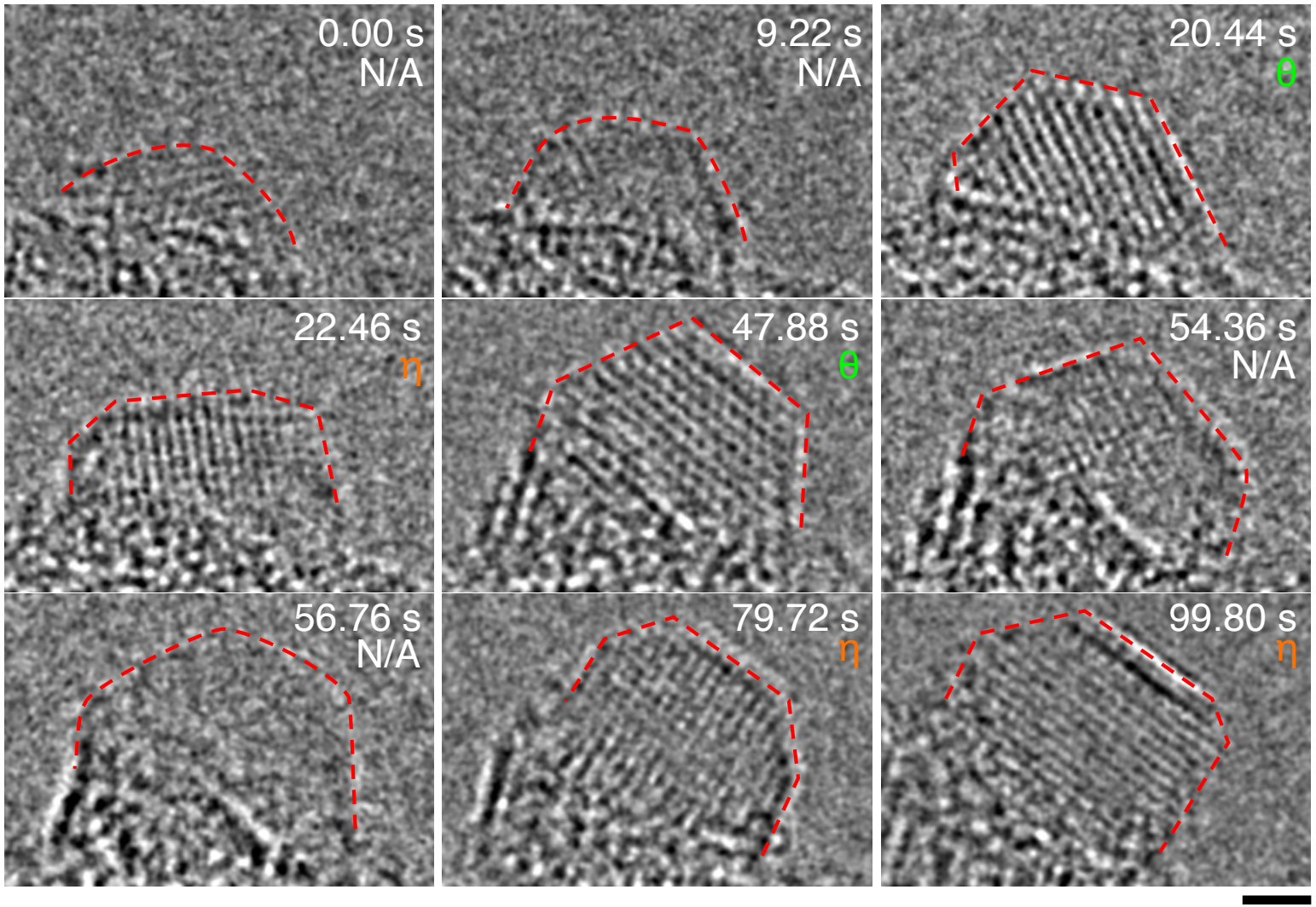
Fluxionality Frozen at Low Temperature

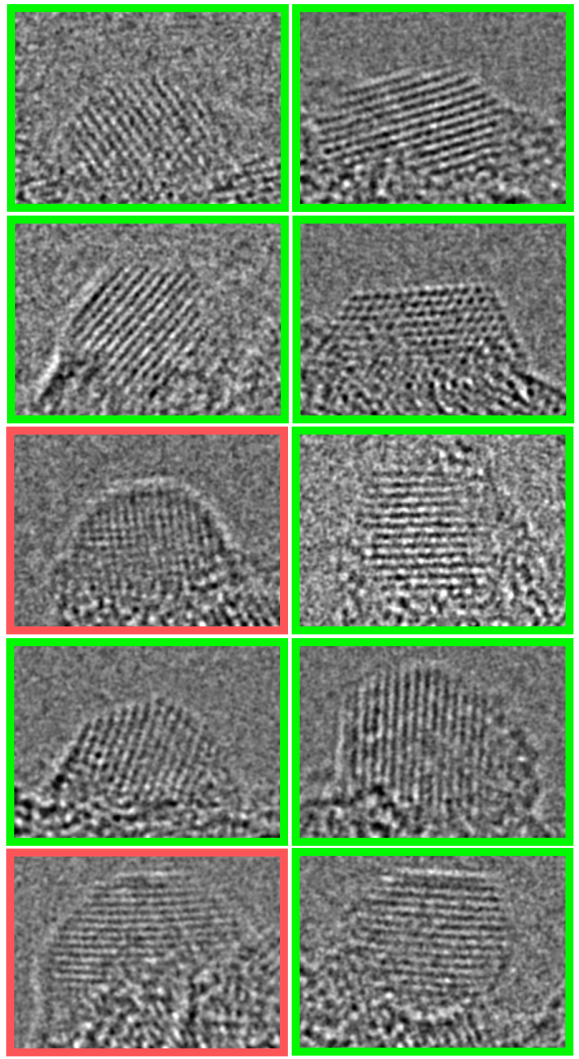
$$r_{\mathrm{c,melt,het}} = \frac{2\gamma T^*}{\Delta H_{\mathrm{f}} \Delta T}$$

T^*: melting point, T: Experimental Temp.

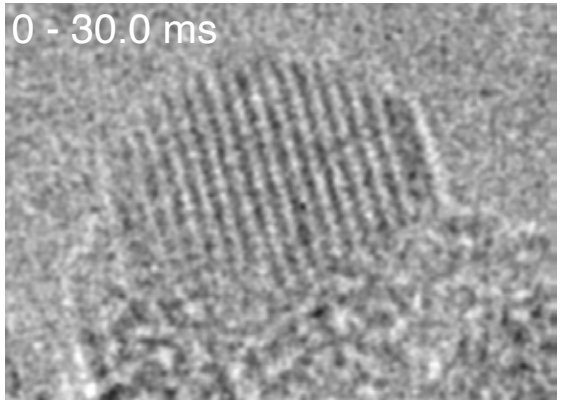
$\Delta T = T^* - T$

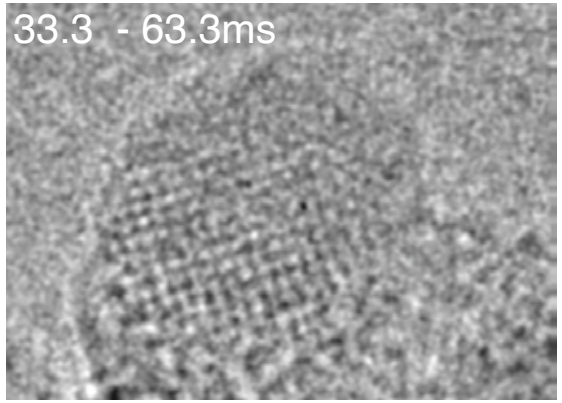
(at 110 K)



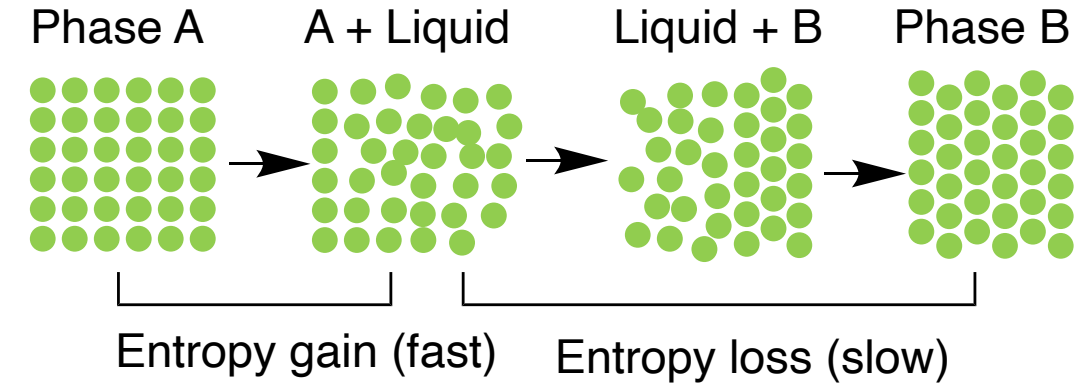


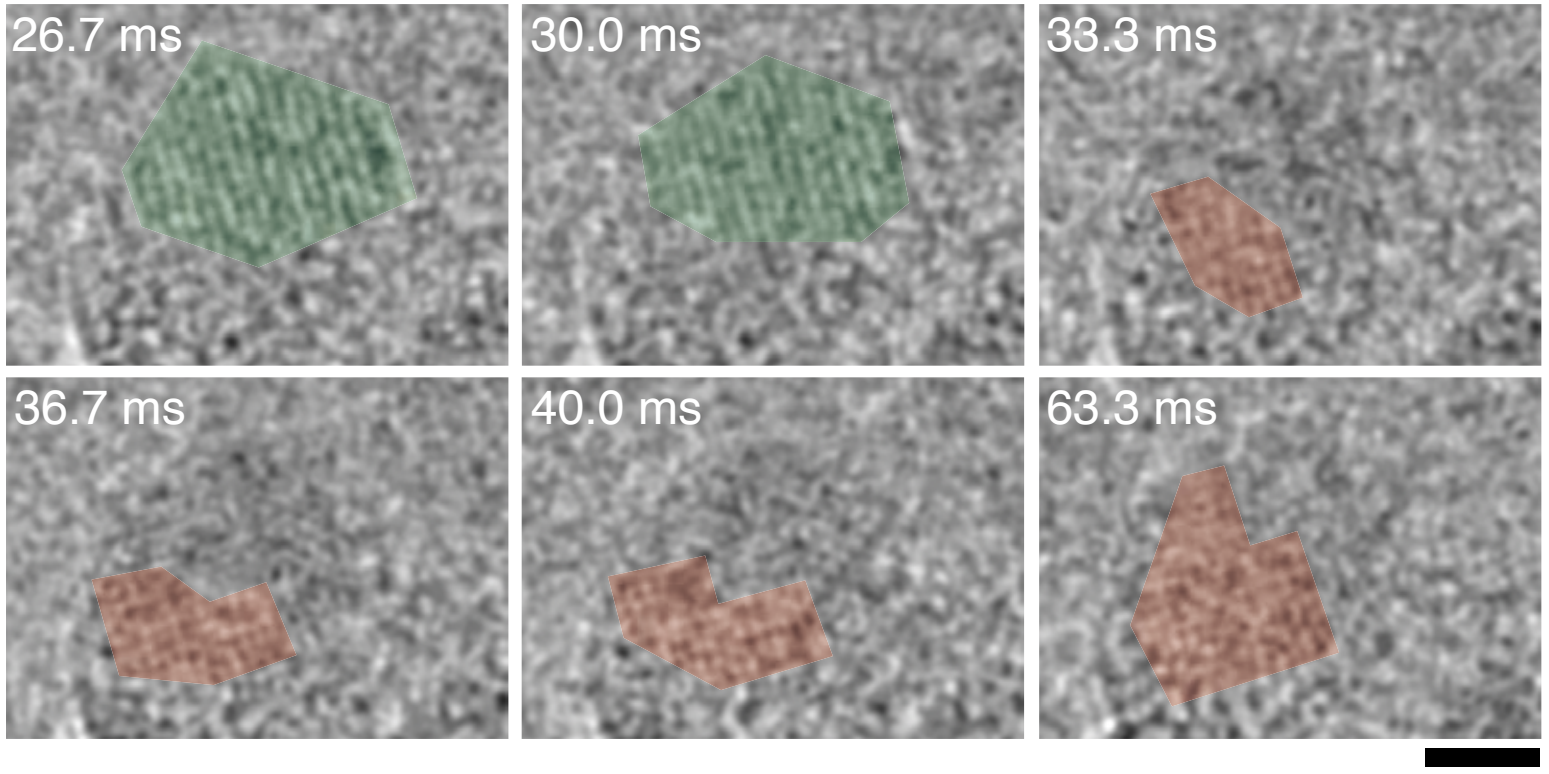
Polymorphic Transition by Fast Observations

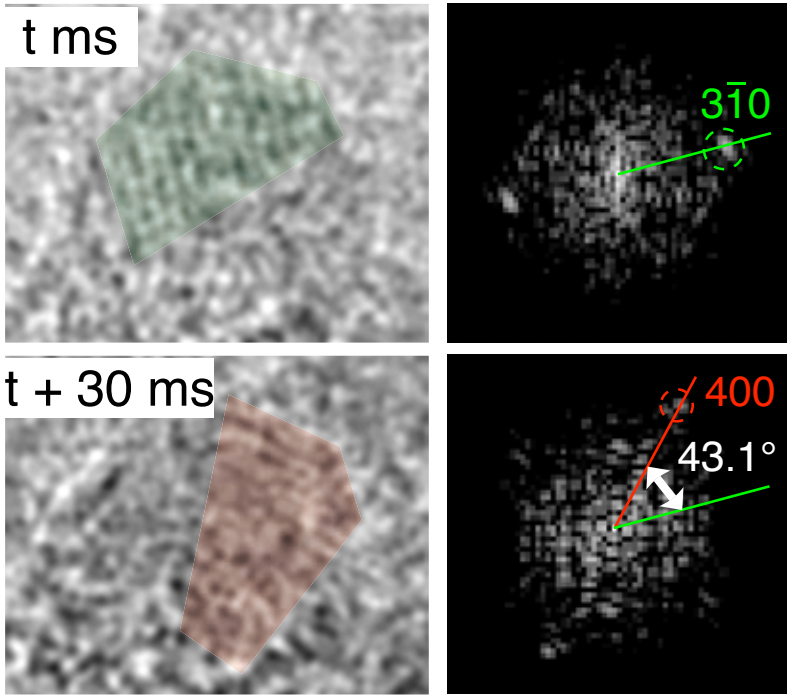




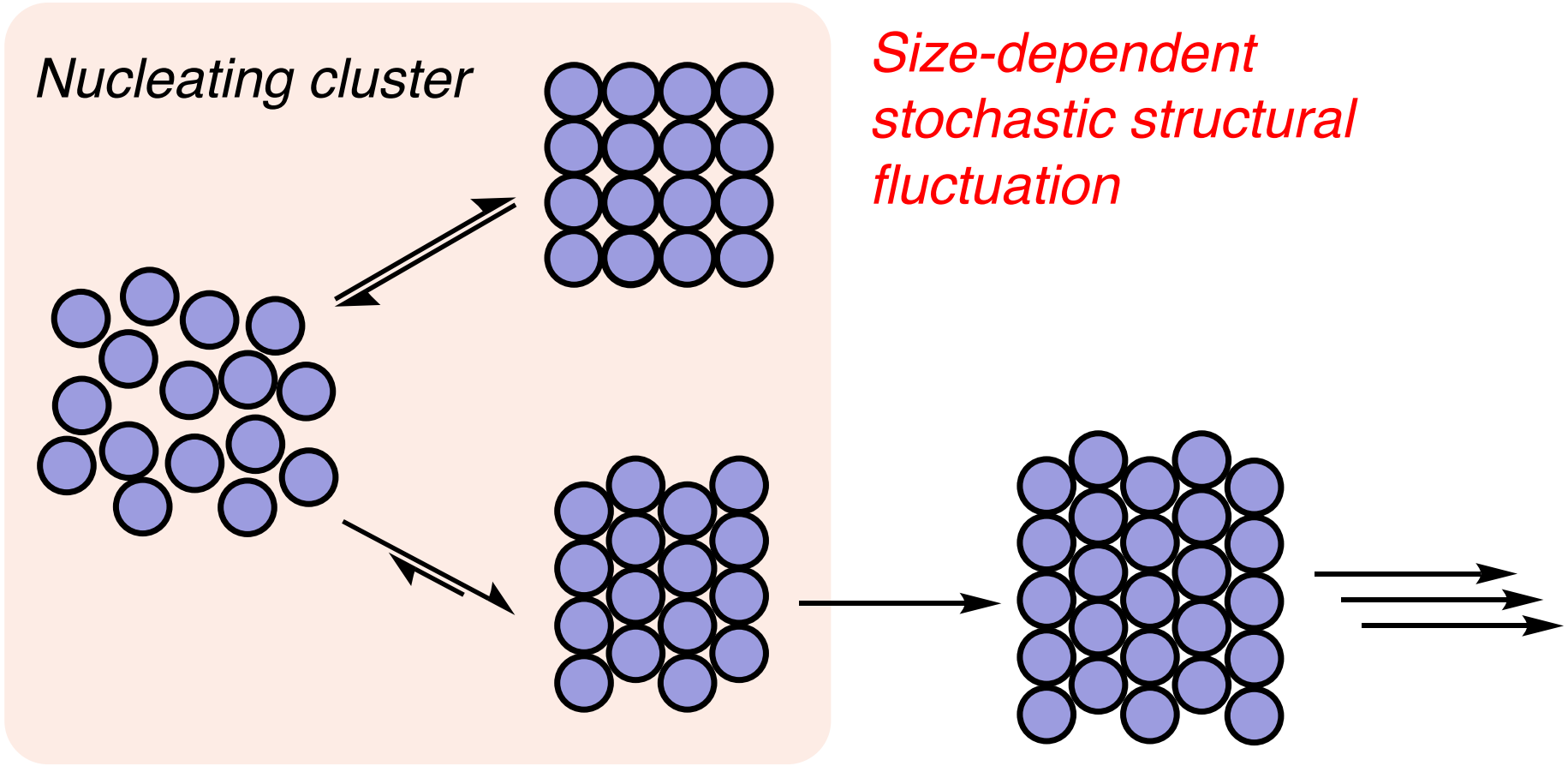
(K3-IS, 300 fps, at 298 K)







Fluxionality during Crystallization

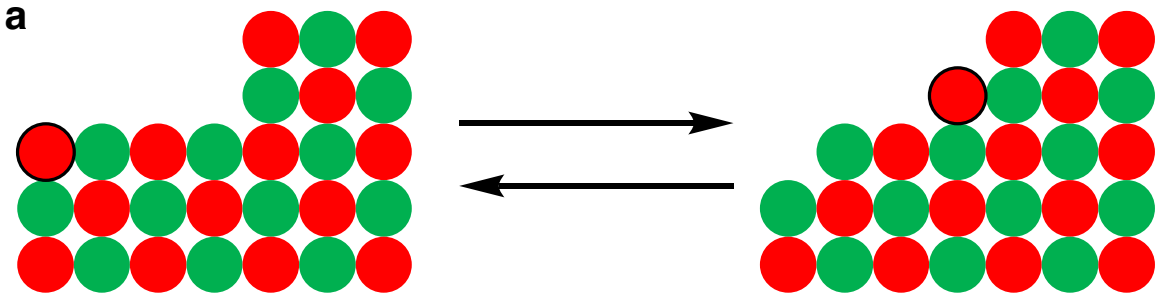


M. Sakakibara *et al.*, *ChemRxiv (10.26434/chemrxiv-2024-g8tl8)*

Fluxionality

V. Fung, D.-e. Jiang, *J. Phys. Chem. C* **2017**, *121*, 10796.
Z. Zhang, B. Zandkarimi, A. N. Alexandrova, *Acc. Chem. Res.* **2020**, *53*, 447.

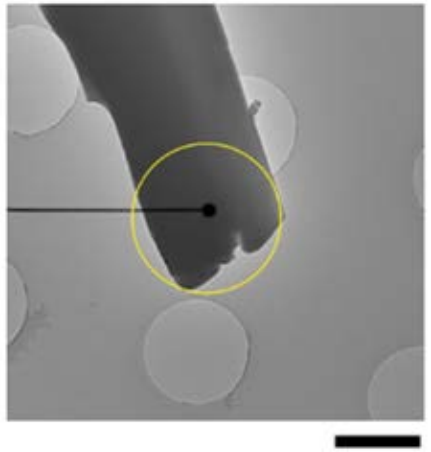
Sub-micrometer: Uniformization of Terrace-Width on CaO

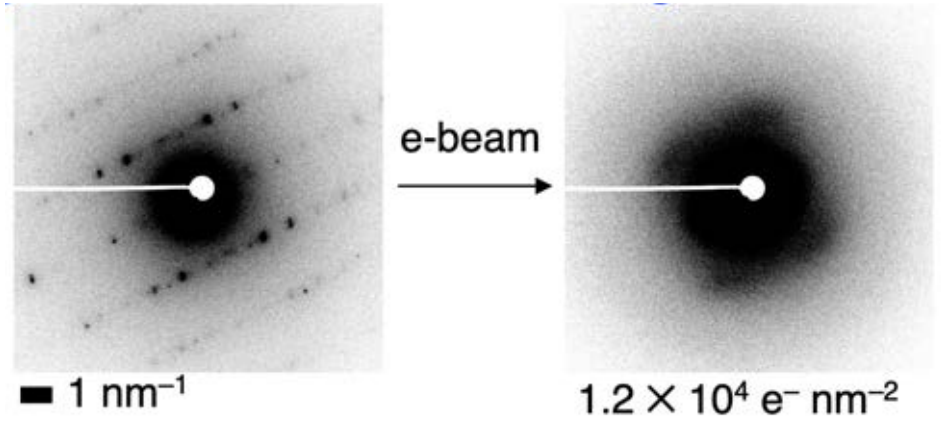


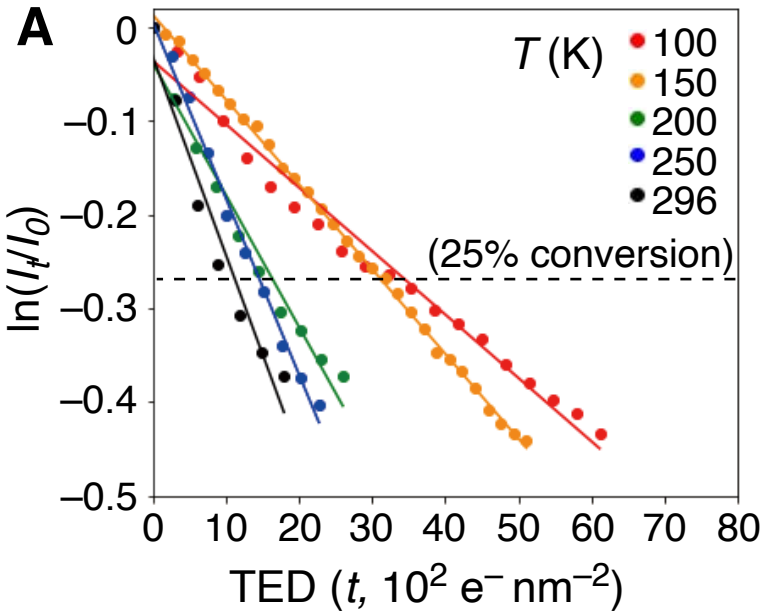
EDR = 6.5 × 10^{7} e^{-} nm^{-2} s^{-1}. OneView-IS.
50 fps. Scale bar: 3 nm. After BP filtering.
RT.

unpublished

Micrometer: Excitation Causes Molecular Disordering in Lattices by ED

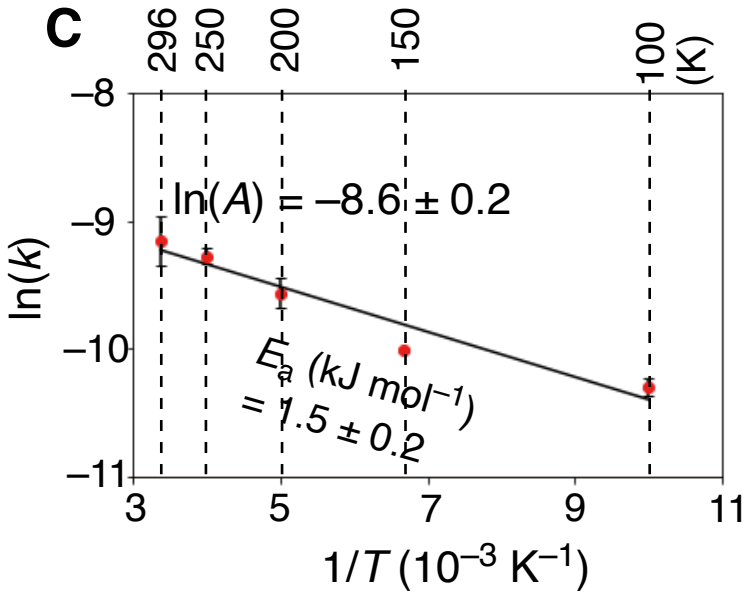






B

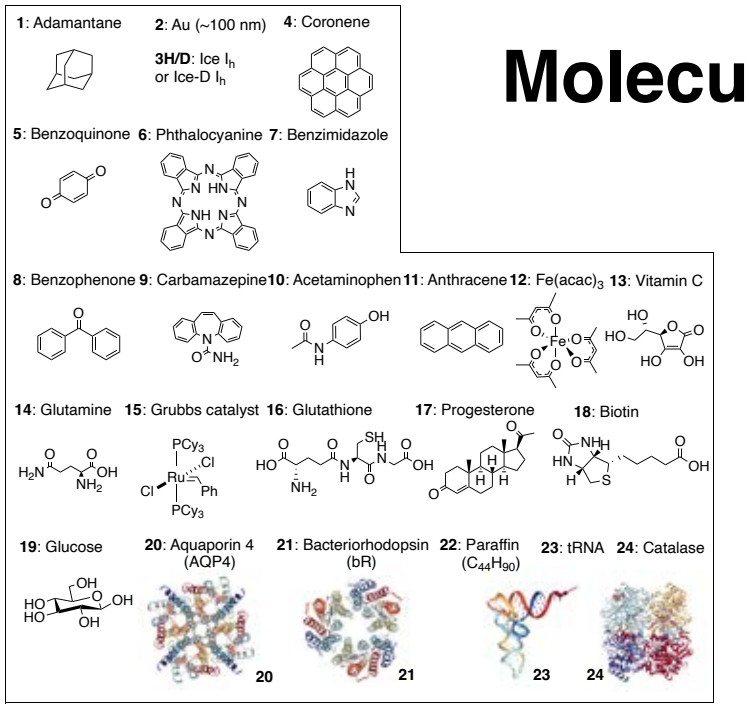
T (K)	k (10^{-4} $(e^-)^{-1}$ nm^2)
100	0.34 ± 0.06
150	0.45 ± 0.01
200	0.70 ± 0.08
250	0.94 ± 0.05
296	1.1 ± 0.2

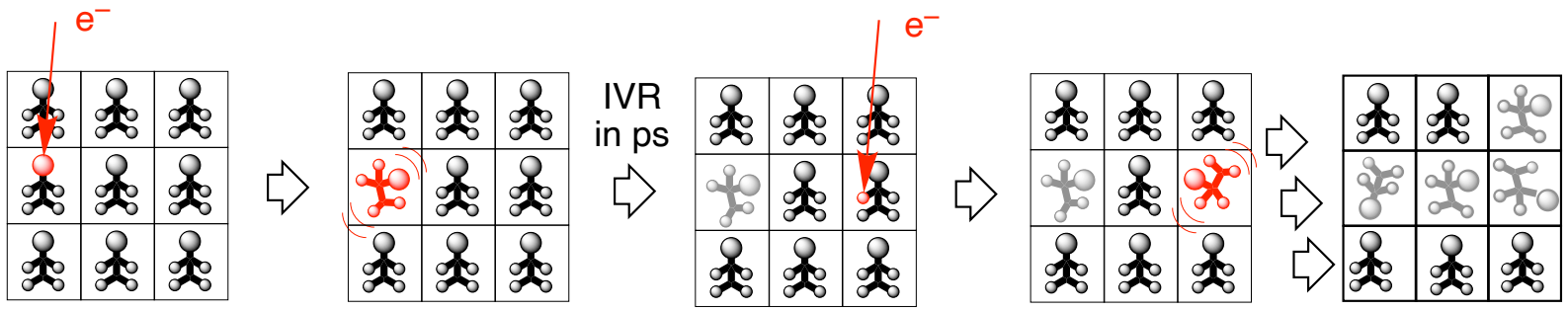


Diffraction intensity $I \propto f^2 \underline{N_{UC}}^2$
(f : structure factor, $\underline{N_{UC}}$: number of UCs)

⇒ $\ln(N_t/N_0) = -k\,\mathrm{TED}$,
TED : total electron dose, N_t: number of ordered molecules

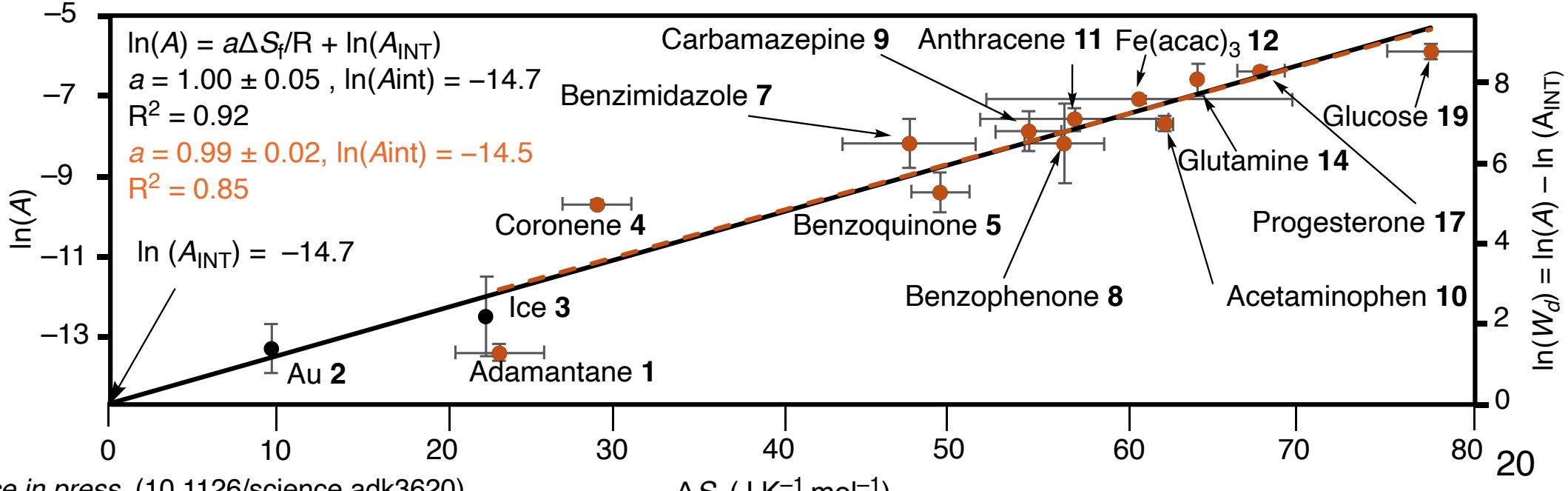
Molecular Disordering Corresponds to Melting in Bulk





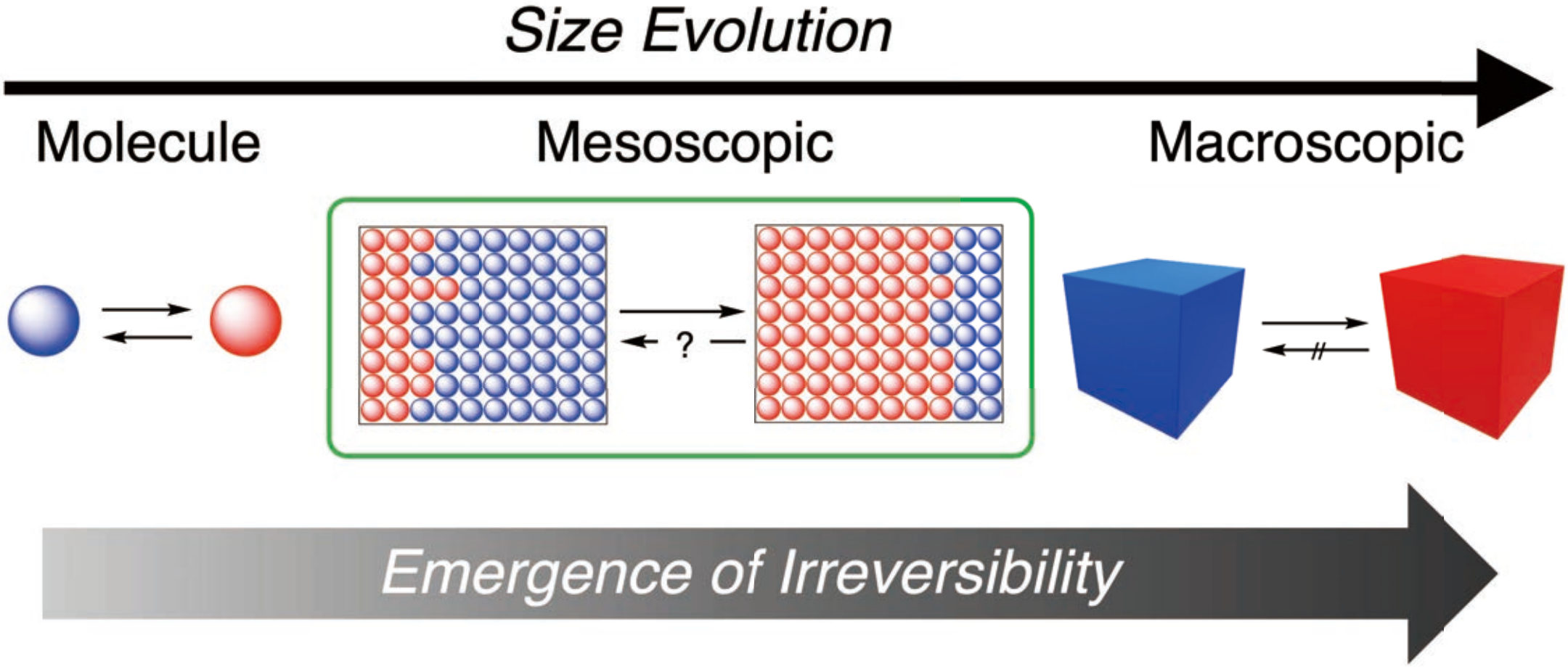
200 keV : λ = 2.5 pm, EDR : ~10^3 e^- nm^{-2} s^{-1}, T : 100-296 K

(IVR: Intramolecular Vibrational energy Redistribution)



D. Liu *et al.*, *Science in press*. (10.1126/science.adk3620)

Conclusion & Perspectives



Establishment of *"Cinematic Chemistry"* will allow us to experimentally explore the relation between deterministic chemical processes in molecular assembly and the stochastic behavior of individual atoms/molecules.

Acknowledgements

University Prof. Eiichi Nakamura
Mr. Masaya Sakakibara (Ph. D. Candidate)
Dr. Dongxin Liu
Mr. Jiarui Fu
Prof. Minoru Hanaya@Gunma U.

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- JST PRESTO

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